

Critical Evaluation and Thermodynamic Optimization of the CaO-P₂O₅ System

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A critical evaluation and thermodynamic optimization of all available experimental data of the CaO-P₂O₅ system was performed to obtain a set of thermodynamic functions which can reproduce all available and reliable experimental phase diagram and thermodynamic data. The modified quasichemical model, which takes into account short range ordering, was employed to describe the thermodynamic properties of the liquid phase. Discrepancies observed in the Gibbs energy of formation of the compounds were resolved and phase diagram and thermodynamic data of all the solid and liquid phases were well reproduced within experimental errors limits including the sharp liquidus of Ca₃(PO₄)₂.

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I. INTRODUCTION

THE CaO-P₂O₅ system is an important key binary system in numerous research fields of industrial interest. This is particularly the case for optical glasses^[1,2] and glasses and glass-ceramics employed as hard tissue implants and drug carriers.^[3–8] The CaO-P₂O₅ system is also important in the steelmaking process to refine phosphorus in molten steel,^[9–11] in cement production,^[12] in phosphate fertilizers,^[13,14] *etc.* To improve current process conditions and develop new processes and products, a good knowledge of its phase diagram and thermodynamic properties is critical. This can be achieved by using the CALPHAD (CALculation of PHADiagram) technique.

In the thermodynamic “optimization” of a system, all available thermodynamic and phase equilibrium data are evaluated simultaneously in order to obtain a set of model equations for the Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. From the Gibbs energy equations, all the thermodynamic properties and phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies in the available data can often be resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner. The thermodynamic database resulting from the optimization can be self-consistently built from low order to high order systems and applied to industrial processes.

In spite of the importance of the CaO-P₂O₅ system, the only attempt to optimize its thermodynamic properties and phase diagram was done recently by Serena *et al.*,^[15,16] who used an associate model to describe the thermodynamic properties of the CaO-P₂O₅ liquid. Several associate species were employed for the liquid phase and the properties of the solid compounds were taken from the compilation of Barin.^[17] Unfortunately, the phases Ca₁₀(PO₄)₆O₂ and Ca₄P₆O₁₉ (trömelite) were ignored, some polymorphic transitions and numerous phase equilibrium and thermodynamic data were not taken into account, and the phase diagram was not well reproduced.

Recently, we performed a new assessment of the thermodynamic properties and phase diagram of pure P₂O₅ to resolve inconsistencies in the SGTE database^[18] and present new thermodynamic data for various solid polymorphs and liquid phases of P₂O₅.^[19] We also performed the thermodynamic optimization of the SiO₂-P₂O₅ system using literature data and new phase diagram experimental data.^[20] In the present study, we have performed the critical evaluation of all the experimental data of the phase diagram and thermodynamic properties of the CaO-P₂O₅ system. This is part of a large research project to develop the thermodynamic database of the Na₂O-CaO-MgO-FeO-Fe₂O₃-MnO-Al₂O₃-SiO₂-P₂O₅ system.

II. REVIEW OF LITERATURE EXPERIMENTAL DATA

A total of eight intermediate compounds are known to exist in the CaO-P₂O₅ binary: Ca₄(PO₄)₂O (C₄P), Ca₁₀(PO₄)₆O₂ (C₁₀P₃), Ca₃(PO₄)₂ (C₃P), Ca₂P₂O₇ (C₂P), Ca₄P₆O₁₉ (C₄P₃), Ca(PO₃)₂ (CP), Ca₂P₆O₁₇ (C₂P₃), and CaP₄O₁₁ (CP₂). Most of these compounds undergo polymorphic transitions. Structural and experimental data relevant to the stability field of each polymorph are detailed in Section II–A below which permits to confirm the existence of each phase. All the non-standard space

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groups were converted into standard notation according to the International Union for Crystallography.^[21] For the sake of clarity, a summary of structural data is given in Table I while melting and polymorphic transition temperatures are reported in Tables II through VI and invariant points involving the liquidus are listed in Table VII. Melting points measured by Dieckmann and Houdremont^[22] were rejected because they are usually much lower than the ones determined in other studies; the presence of water and impurities is probably the source of error. The phase diagram of the CaO-P₂O₅ system is shown in Figure 1 with experimental data. Phase equilibrium and thermodynamic data are reviewed in Sections II-B and II-C, respectively.

A. Structural Data and Phase Transformations of Compounds

1. Ca₄(PO₄)₂O (C₄P)

Ca₄(PO₄)₂O was discovered by Hilgenstock^[23] in slags from Hörde (Wesphalia). It is sometimes named hilgenstockite, which is not recognized as an official mineral name.^[24] Ca₄(PO₄)₂O exists in two polymorphic forms. The high temperature form, α-Ca₄(PO₄)₂O, has an orthorhombic structure^[23,25–31] and crystallizes in the P222₁^[28,29] or P2₁2₁2^[30,31] space group. The only discordant result is from Schneiderhohn^[32] who reported that it belongs to the triclinic system based on optical microscopic observations. The low temperature form, β-Ca₄(PO₄)₂O, was first thought to crystallize in the orthorhombic^[27] and triclinic^[33] systems but it is now known to belong to the monoclinic P2₁ space group.^[30,31,34]

The first experimental studies^[35–38] report that α-Ca₄(PO₄)₂O melts congruently while the most recent ones^[39–41] state that it melts peritectically. More credit is given to the last two studies^[40, 41] because they employed an *in situ* (heating microscopy) technique to measure the melting point, which is observed at 1983 K to 1993 K (1710 °C to 1720 °C). According to Cieřla^[31] and Cieřla and Rudnicki,^[42] the transition between α and β occurs in the temperature range of 873 K to 943 K (600 °C to 670 °C). Melting temperatures reported in the literature are presented in Table II together with the temperatures of the α-β polymorphic transition.

2. Ca₁₀(PO₄)₆O₂ (C₁₀P₃; Oxyapatite)

The existence of oxyapatite, Ca₁₀(PO₄)₆O₂, has been debated for a long time (see Trombe and Montel^[43] for a review), but it is now recognized as a valid species due to the work of Trombe and Montel^[43–45] and Trombe,^[46] who used X-ray diffraction (XRD), thermogravimetric analysis (TGA), infrared spectroscopy (IR), and chemical analysis to characterize it. The structure was only determined recently by Henning *et al.*^[47] with the help of high-resolution electron microscopy (HREM): it is hexagonal and belongs to the P6 space group. In their first publications,^[44–46] Trombe and Montel place the stability field of oxyapatite between 1073 K and 1273 K (800 °C and 1000 °C), while in the later,^[43] they put it between 1123 K and 1323 K (850 °C and 1050 °C) (Table II).

3. Ca₃(PO₄)₂ (C₃P)

Ca₃(PO₄)₂, and more specifically β-Ca₃(PO₄)₂, are sometimes named whitlockite or Ca-whitlockite, a mineral found in the Palermo quarry, New Hampshire (USA). The mineral was first described by Frondel^[48] as Ca₃(PO₄)₂ based on chemical analysis. Later, Frondel^[49] showed that Ca-whitlockite and synthetic β-Ca₃(PO₄)₂ are the same phase due to their identical XRD patterns and optical constants. Currently, whitlockite is rather considered as a mineral with the general chemical formula Ca₉(Mg, Fe²⁺)(PO₄)₆(PO₃OH).^[24,50]

Ca₃(PO₄)₂ exists in three polymorphic forms. The high temperature phase, α'-Ca₃(PO₄)₂, was investigated by high-temperature neutron diffraction by Knowles *et al.*^[51] and Yashima and Sakai^[52] who determined that it belongs to the hexagonal P6₃/mmc and trigonal P3m1 space groups, respectively. According to Mackay,^[53] Mathew *et al.*^[54] and Yashima and Sakai,^[52] the intermediate temperature phase, α-Ca₃(PO₄)₂, crystallizes in the monoclinic space group P2₁/c. Frondel^[48] determined by XRD that the low temperature polymorph, β-Ca₃(PO₄)₂, belongs to the trigonal system and probably to the R3c space group; using XRD, Mackay^[55] found the same space group. The structure was later refined by Dickens *et al.*^[56] and Calvo and Gopal^[57] using XRD and Yashima *et al.*^[58] using neutron diffraction and the belonging to the trigonal system was confirmed but the space group was changed to R3c. Based on luminescence and calorimetric measurements at low temperatures, Koelmans *et al.*^[59] identified two additional phase transformations between 233 K and 308 K (−40 °C and 35 °C). Unfortunately, due to the sluggishness of these transitions, they were unable to resolve them. According to Koelmans *et al.*,^[59] the transformations might be related to some cation ordering in the structure; they are not taken in consideration in the present optimization.

The α'-Ca₃(PO₄)₂ phase melts congruently. In general, the earliest studies (Table III) report rather low melting temperatures [*e.g.*, 1823 K (1550 °C)] while the most recent ones give high melting temperatures [*e.g.*, 2083 K (1810 °C)]; our preference went to the most recent investigations.

Temperatures reported in the literature for the polymorphic transitions are summarized in Table III. Remarkably, the whole spectrum of transition temperatures lies between 1553 K and 1813 K (1280 °C and 1540 °C) for the α'-α transition and between 1273 K and 1773 K (1000 °C and 1500 °C) for the α-β one. Fasting and Haraldsen^[60] and Ando^[61] were the first to point out these differences and to propose that small amounts of impurities can change considerably the transition temperature of α- to β-Ca₃(PO₄)₂. Their experiments show that a small addition of Na₂O or BaO to Ca₃(PO₄)₂ decreases the transition temperature by stabilizing the α phase while a small addition of MgO, FeO or SiO₂ increases the transition temperature by stabilizing the β phase. Among the oxides investigated, the effect of MgO is the most intense one. This later observation is corroborated by numerous studies.^[56,62–67] On the other hand, Bredig *et al.*^[68] showed that very small amounts of moisture and excess CaO can modify

Table I. Structural Data of the Polymorphs Present in the CaO-P₂O₅ System

Phase	Crystal System	Space Group	Technique	Reference
α -Ca ₄ (PO ₄) ₂ O	orthorhombic		OM	Hilgenstock ^[23]
	orthorhombic		OM	von Groddeck and Broockmann ^[25]
	orthorhombic		OM	Bücking and Linck ^[26]
	orthorhombic		G	Miers ^[27]
	triclinic		OM	Schneiderhohn ^[32]
	orthorhombic	<i>P</i> 222 ₁	XRD	Trömel and Zaminer ^[28]
	orthorhombic	<i>P</i> 222 ₁	XRD	Bauer and Balz ^[29]
	orthorhombic	<i>P</i> 2 ₁ 2 ₁ 2	XRD	Brown and Epstein ^[30]
β -Ca ₄ (PO ₄) ₂ O	orthorhombic	<i>P</i> 2 ₁ 2 ₁ 2	HTXRD	Cieśla ^[31]
	orthorhombic		G	Miers ^[27]
	monoclinic		G	Termier and Richard ^[187]
	triclinic		OM	Schleede <i>et al.</i> ^[33]
	monoclinic	<i>P</i> 2 ₁	XRD	Brown and Epstein ^[30]
	monoclinic	<i>P</i> 2 ₁	XRD	Dickens <i>et al.</i> ^[34]
	monoclinic	<i>P</i> 2 ₁	HTXRD	Cieśla ^[31]
	hexagonal	<i>P</i> 6̄	HREM	Henning <i>et al.</i> ^[47]
Ca ₁₀ (PO ₄) ₆ O ₂	hexagonal	<i>P</i> 6 ₃ / <i>mmc</i>	HTND	Knowles <i>et al.</i> ^[51]
α' -Ca ₃ (PO ₄) ₂	trigonal	<i>P</i> 3̄ <i>m</i> 1	HTND	Yashima and Sakai ^[52]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Mackay ^[53]
α -Ca ₃ (PO ₄) ₂	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Mathew <i>et al.</i> ^[54]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	HTND	Yashima and Sakai ^[52]
	trigonal	<i>R</i> 3̄ <i>c</i>	XRD	Frondel ^[48]
	trigonal	<i>R</i> 3̄ <i>c</i>	XRD	Mackay ^[55]
β -Ca ₃ (PO ₄) ₂	trigonal	<i>R</i> 3̄ <i>c</i>	XRD	Dickens <i>et al.</i> ^[56]
	trigonal	<i>R</i> 3̄ <i>c</i>	XRD	Calvo and Gopal ^[57]
	trigonal	<i>R</i> 3̄ <i>c</i>	XRD	Yashima <i>et al.</i> ^[58]
	trigonal	<i>R</i> 3̄ <i>c</i>	ND	Ranby <i>et al.</i> ^[80]
	trigonal	<i>R</i> 3̄ <i>c</i>	XRD	Calvo ^[81]
α -Ca ₂ P ₂ O ₇	orthorhombic		XRD	Schneiderhohn ^[32]
β -Ca ₂ P ₂ O ₇	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Corbridge ^[82]
	tetragonal	<i>P</i> 4 ₁	XRD	Keppeler ^[83]
	tetragonal	<i>P</i> 4 ₁	XRD	Webb ^[84]
	tetragonal	<i>P</i> 4 ₁	XRD	Schneider <i>et al.</i> ^[86]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Boutin <i>et al.</i> ^[85]
	tetragonal	<i>P</i> 4 ₁	XRD	
γ -Ca ₂ P ₂ O ₇	unknown			
Ca ₄ P ₆ O ₁₉	triclinic		XRD	Wieker <i>et al.</i> ^[97]
	triclinic	<i>P</i> 1̄	XRD	Höppe ^[99]
α -Ca(PO ₃) ₂	hexagonal		OM	Schneiderhohn ^[32]
	monoclinic	<i>C</i> <i>c</i>	NMR, XRD	Weil <i>et al.</i> ^[104]
β -Ca(PO ₃) ₂	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Corbridge ^[105]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Rothammel and Burzlaff ^[106]
	monoclinic		HTXRD	Viting <i>et al.</i> ^[107]
	monoclinic	<i>C</i> <i>c</i>	XRD	Jackson <i>et al.</i> ^[109]
δ -Ca(PO ₃) ₂	tetragonal		XRD	Bale <i>et al.</i> ^[90]
Ca ₂ P ₆ O ₁₇	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Stachel ^[111]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Meyer <i>et al.</i> ^[112]
α -CaP ₄ O ₁₁	orthorhombic	<i>A</i> <i>e</i> <i>a</i> 2	HTXRD	Schneider ^[113]
	orthorhombic		HTXRD	Viting <i>et al.</i> ^[107]
β -CaP ₄ O ₁₁	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Beucher ^[114]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Tordjman <i>et al.</i> ^[115]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	XRD	Meyer <i>et al.</i> ^[112]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	HTXRD	Schneider ^[113]
	monoclinic	<i>P</i> 2 ₁ / <i>c</i>	HTXRD	Viting <i>et al.</i> ^[107]

G: goniometer; HREM: high-resolution electron microscopy; HTND: high-temperature neutron diffraction; HTXRD: high-temperature X-ray diffraction; NMR: nuclear magnetic resonance; OM: optical microscopy; XRD: X-ray diffraction.

the temperature of the polymorphic transformation. By taking in consideration these observations, our preference went to the α' - α and α - β transitions data located around 1743 K and 1398 K (1470 °C and 1125 °C), respectively.

Other phase transitions were reported for Ca₃(PO₄)₂: one at 1687 K (1414 °C),^[69] one at 1681 K (1408 °C),^[70] one at 1623 K (1350 °C),^[71–74] one at 1603 K (1330 °C),^[69] one at 1326 K (1103 °C),^[70,72,73] one at 1370 K (1097 °C),^[69] one at 1313 K (1040 °C),^[74] and

Table II. Melting and Polymorphic Transition Temperatures of $\text{Ca}_4(\text{PO}_4)_2\text{O}$ (C_4P) and $\text{Ca}_{10}(\text{PO}_4)_6\text{O}_2$ (C_{10}P_3)

Compound	Transition	Temperature [K (°C)]	Technique ¹	Comment	Reference
$\text{Ca}_4(\text{PO}_4)_2\text{O}$	$\text{CaO} + \text{Liq} = \alpha\text{-C}_4\text{P}$	2143 (1870)	QM	congruent melting: $\text{Liq} = \alpha\text{-C}_4\text{P}$	Blome ^[35]
		1973 (1700)	TA, OM, XRD	congruent melting: $\text{Liq} = \alpha\text{-C}_4\text{P}$	Trömel ^[36]
		2033 (1760)	TA	congruent melting: $\text{Liq} = \alpha\text{-C}_4\text{P}$	Behrendt and Wentrup ^[37]
		1973 (1700)	QM, OM, XRD	congruent melting: $\text{Liq} = \alpha\text{-C}_4\text{P}$	Barrett and McCaughey ^[38]
		1913 (1640)	TA	peritectic: $\text{CaO} + \text{Liq} = \alpha\text{-C}_4\text{P}$	Trömel ^[39]
	$\alpha \leftrightarrow \beta$	1983 (1710)	HM	peritectic: $\text{CaO} + \text{Liq} = \alpha\text{-C}_4\text{P}$	Trömel and Fix ^[40]
		1993 (1720)	HM	peritectic: $\text{CaO} + \text{Liq} = \alpha\text{-C}_4\text{P}$	Welch and Gutt ^[41]
		2021 (1748)	Optimized	peritectic: $\text{CaO} + \text{Liq} = \alpha\text{-C}_4\text{P}$	this work
		873 to 943 (600 to 670)	DTA, TGA, HTXRD		Cieślak ^[31]
		873 to 943 (600 to 670)	DTA, TGA, DTG, TD, HTXRD, XRD		Cieśla and Rudnicki ^[42]
$\text{Ca}_{10}(\text{PO}_4)_6\text{O}_2$	$\alpha\text{-C}_4\text{P} + 2\beta\text{-C}_3\text{P} = \text{C}_{10}\text{P}_3$	908 (635)	optimized		this work
		1273 (1000)	TGA, IR, XRD, CA		Trombe and Montel ^[44,45] Trombe ^[46]
		1323 (1050)	TGA, IR, XRD, CA		Trombe and Montel ^[43]
	$\text{C}_{10}\text{P}_3 = \alpha\text{-C}_4\text{P} + 2\beta\text{-C}_3\text{P}$	1323 (1050)	optimized		this work
		1073 (800)	TGA, IR, XRD, CA		Trombe and Montel ^[44,45] Trombe ^[46]
		1123 (850) 1126 (853)	TGA, IR, XRD, CA optimized		Trombe and Montel ^[43] this work

CA: chemical analysis; DTA: differential thermal analysis; DTG: differential thermogravimetry; HM: heating microscopy; IR: infrared red spectroscopy; QM: quenching method; TA: thermal analysis; TD: thermogravimetry; TGA: thermogravimetric analysis; other abbreviations see Table I.

one at 1283 K (1010 °C),^[69,74] all using thermal analysis and XRD. Each transition is considered as minor by the authors and might be due to the purity of the starting materials; consequently, none of them are considered here. Recently, Belik *et al.*^[75] reported a new transition at 1193 K (920 °C) using electrical-conductivity measurements. No other details are reported for this transformation and for this reason it is also discarded.

Solid solution was initially reported for the α' -, α -, and β - C_3P phases in the $\text{CaO-P}_2\text{O}_5$ system by Welch and Gutt^[41] but a careful XRD study performed by Kreidler and Hummel^[76] showed that tricalcium phosphate is stoichiometric; according to them, loss of P_2O_5 probably occurred during Welch and Gutt's experiments. This diagnostic was confirmed by Wallace and Brown^[77] who heated some $\text{CaO-P}_2\text{O}_5$ mixtures ranging from about 0.25 to 0.33 mol fraction P_2O_5 at 973 K and 1173 K (700 °C and 900 °C) and found no solid solution in the C_3P phase. For Berak and Znamierowska,^[72] who used thermal analysis, and Riboud,^[78] who employed the quenching method, no solid solution was observed either. Recently, Jungowska^[79] also reported some solid solution in α - and β - $\text{Ca}_3(\text{PO}_4)_2$ using the quenching method and XRD but P_2O_5 loss may have occurred during their rather long (3 to 170 hours) experiments in open crucibles between 1173 K and 1523 K (900 °C and 1250 °C).

4. $\text{Ca}_2\text{P}_2\text{O}_7$ (C_2P)

The compound $\text{Ca}_2\text{P}_2\text{O}_7$ exists in three polymorphic forms. The high temperature polymorph, $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$, was studied by Ranby *et al.*^[80] and Calvo^[81] using XRD. The first study reports that it crystallizes in the orthorhombic system while the second one assigns it to the monoclinic space group $P2_1/c$. The intermediate form, $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, was first investigated by Schneiderhohn.^[32] He performed optical microscopic observations on crystals and deduced that they belong to the tetragonal system. This diagnostic was confirmed by XRD studies made by Corbridge,^[82] Keppler,^[83] Webb,^[84] and Boutin *et al.*^[85] who determined that $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ crystallizes in the tetragonal space group $P4_1$. For Schneider *et al.*^[86] though, X-ray data rather indicate that this phase belongs to the monoclinic space group $P2_1/c$. The structure of the low temperature form, $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$, is not known yet. McIntosh and Jablonski^[87] and Parodi *et al.*^[88] measured its X-ray pattern but they did not determine the structure. Recently, Cornilsen and Condrate^[89] shown that the Raman and X-ray patterns of $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$ are similar to, but well less defined than $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, which suggests that both phases are structurally related.

A large consensus exists for the melting point of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$. In the most recent studies,^[40,41,72,73,90-94] it is systematically detected around 1623 K (1350 °C; see Table IV). The α - β transition (Table IV) was observed over the temperature range of 1173 K to 1523 K (900 °C to 1250 °C) and clusters around 1448 K (1175 °C). For the β - γ transition, the temperature ranges between 828 K and 1473 K (555 °C and 1200 °C), but most data lie between 900 K and 1123 K (627 °C and 850 °C).

Table III. Melting and Polymorphic Transition Temperatures of $\text{Ca}_3(\text{PO}_4)_2$ (C_3P)

Transition	Temperature [K (°C)]	Technique	Comment	Reference	
Liq = α'	1823 (1550)	TA		Nielsen ^[117]	
	1853 (1580)	QM, XRD		Bredig ^[188]	
	2003 (1730)	TA, OM, XRD		Trömel ^[36]	
	2063 (1790)	TA		Behrendt and Wentrup ^[37]	
	1973 (1700)	QM, OM, XRD		Barrett and McCaughey ^[38]	
	1993 (1720)	QM, XRD		Bale <i>et al.</i> ^[90]	
	2003 ± 10 (1730 ± 10)	CFM		St. Pierre ^[189, 190]	
	1998 (1725)	QM, OM, TA, XRD		Wojciechowska <i>et al.</i> ^[137]	
	1993 (1720)	VP		Guérin <i>et al.</i> ^[191]	
	2003 (1730)	OM, HTXRD		Bobrownicki and Slawski ^[192]	
	2029 (1756)	HM, HTXRD		Nurse <i>et al.</i> ^[193]	
	1988 (1715)	TA, OM, XRD		Berak ^[194]	
	2083 (1810)	QM		Trömel and Fix ^[40]	
	2050 (1777)	HM	if P_2O_5 loss is considered; see Kreidler and Hummel ^[76]	Welch and Gutt ^[41]	
	2073 (1800)	HTXRD		Fix <i>et al.</i> ^[195]	
	2058 (1785)	DTA, OM, XRD		Shirvinskaya and Bondar ^[196]	
	2083 (1810)	DTA, OM, TD, XRD		Berak and Czupińska ^[71]	
	$\alpha' \leftrightarrow \alpha$	2076 (1803)	optimized		this work
		1673 (1400)	TA, OM, XRD	correspond to their $\alpha = \beta$ transition	Trömel ^[36]
1743 (1470)		TA		Behrendt and Wentrup ^[37]	
1673 (1400)		TA	correspond to their $\alpha = \beta$ transition	Trömel ^[39]	
1703 (1430)		HM, HTXRD		Nurse <i>et al.</i> ^[193, 197]	
~1703 (~1430)		TA, OM, XRD		Berak ^[198]	
1740 to 1748 (1467 to 1475)		TA, XRD		Trömel and Fix ^[40]	
1703 (1430)		HM		Welch and Gutt ^[41]	
1553 (1280)		DTA, HTXRD		Ando and Matsuno ^[199]	
1743 (1470)		HTXRD		Fix <i>et al.</i> ^[76]	
1748 ± 7 (1475 ± 7)		DTA		Kreidler ^[200]	
1763 (1490)		TA		Berak and Tomczak-Hudyma ^[69]	
1743 (1470)		TA, XRD		Berak and Znamierowska ^[72, 73]	
1763 (1490)		TA, XRD		Berak and Tomczak-Hudyma ^[74]	
~1743 (~1470)		EMF	polymorphs not identified	Fisher <i>et al.</i> ^[201]	
1703 (1430)		DTA, OM, XRD		Shirvinskaya and Bondar ^[196]	
1707 (1434)		DTA, XRD	correspond to their $\alpha'' = \alpha'$ transition	Millet <i>et al.</i> ^[70]	
1743 (1470)		DTA, OM, TD, XRD		Berak and Czupińska ^[71]	
1693 to 1723 (1420 to 1450)		DTA, TGA, DTG, TD, HTXRD, XRD		Cieśla and Rudnicki ^[42]	
1713 to 1743 (1440 to 1470)		DTA, TGA, DTG, TD, HTXRD, XRD		Cieśla and Rudnicki ^[202]	
1703 (1430)		DTA, TGA, IR, HTXRD, XRD		Zhou <i>et al.</i> ^[203]	
1813 (1540)		TGA, XRD, IR, CA		Aoki ^[204]	
1748 (1475)		XRD		De Aza <i>et al.</i> ^[205]	
~1773 (~1500)		HTND		Knowles <i>et al.</i> ^[51]	
1731 to 1781 (1458 to 1508)		HTND		Yashima and Sakai ^[52]	
1758 (1485)		DTA		Carrodeguas <i>et al.</i> ^[206]	
1743 (1470)		DTA, TGA, XRD		Martínez <i>et al.</i> ^[207]	
1748 (1475)		optimized		this work	
$\alpha \leftrightarrow \beta$		1453 (1180)	QM, XRD		Bredig ^[188]
	1523 to 1773 (1250 to 1500)	OM	crystals made by Trömel ^[36]	Schneiderhohn ^[32]	
	1373 (1100)	TA		Britzke and Veselovskii ^[144]	
	1623 (1350)	QM, XRD		Bale <i>et al.</i> ^[90]	
	1388 (1115)	not mentioned	probably QM, OM, XRD	Hill <i>et al.</i> ^[208]	
	1473 (1200)	QM, TA, XRD		Trömel <i>et al.</i> ^[209]	
	1423 (1150)	QM, XRD		McIntosh and Jablonski ^[87]	
	1343 (1070)	QM, OM, TA, XRD	rapidly quenched samples	Wojciechowska <i>et al.</i> ^[137]	
	1453 (1180)	TA		Ando ^[210]	
	1398 (1125)	HM, HTXRD		Nurse <i>et al.</i> ^[193, 197]	
	1423 (1150)	TA, OM, XRD		Berak ^[194]	
	1403 (1130)	DTA		Sarver <i>et al.</i> ^[211]	
	1433 (1160)	DTA		Bauer ^[212]	
	1408 (1135)	DTA, TGA, XRD		Kubicki ^[213]	
	1453 (1180)	DTA, HTXRD		Ando and Matsuno ^[199]	
	1393 (1120)	HTXRD		Fix <i>et al.</i> ^[76]	
	1423 (1150)	TA		Berak and Tomczak-Hudyma ^[69]	

Table III. continued

Transition	Temperature [K (°C)]	Technique	Comment	Reference
	1423 (1150)	TA, XRD		Berak and Znamierowska ^[72,73]
	1473 (1200)	TA, XRD		Berak and Tomczak-Hudyma ^[74]
	~1473 (~1200)	EMF	polymorphs not identified	Fisher <i>et al.</i> ^[201]
	1390 (1117)	HTXRD		Madsen in Boell <i>et al.</i> ^[214]
	1493 (1220)	DTA, XRD		Millet <i>et al.</i> ^[70]
	1408 (1135)	IM, XRD		Monma and Goto ^[215]
	1439 (1166)	DTA, XRD		Monma and Goto ^[215]
	1403 to 1425 (1130 to 1152)	DTA, TGA, IR, XRD		Cieśla and Rudnicki ^[216]
	1423 (1150)	DTA, XRD, OM, TD		Berak and Czupińska ^[71]
	1433 to 1523 (1160 to 1250)	DTA, TGA, DTG, TD, HTXRD, XRD		Cieśla and Rudnicki ^[202]
	1423 (1150)	DTA, TGA, IR, HTXRD, XRD		Zhou <i>et al.</i> ^[203]
	1563 (1290)	TGA, XRD, IR, CA		Aoki ^[204]
	>1473 (>1200)	QM, XRD, SEM, EDS		Famery <i>et al.</i> ^[217]
	1423 (1150)	XRD		De Aza <i>et al.</i> ^[205]
	1273 to 1523 (1000 to 1250)	HTXRD		Gibson <i>et al.</i> ^[62]
	~1573 (~1300)	HTND		Knowles <i>et al.</i> ^[51]
	1423 (1160)	DTA		Gibson <i>et al.</i> ^[218]
	>1473 (>1200)	DTA, TGA, XRD		Jinlong <i>et al.</i> ^[219]
	1393 (1120)	DTA, XRD		Jungowska ^[79]
	1408 (1135)	ECM		Belik <i>et al.</i> ^[75]
	~1473 (~1200)	QM, XRD, TD		Ryu <i>et al.</i> ^[220]
	1423 (1150)	DTA, TGA, DTG, XRD		Pan <i>et al.</i> ^[63]
	1423 (1150)	DTA		Enderle <i>et al.</i> ^[64]
	1423 (1150)	QM, DTA, XRD	correspond to their $\alpha = \beta'$ transition	Goetz-Neunhoeft ^[221]
	1467 (1194)	DSC, TGA, XRD		Maciejewski <i>et al.</i> ^[120]
	1388 (1115)	HTND		Carrodegua ^[65]
	1438 (1165)	DTA		Carrodegua <i>et al.</i> ^[206]
	1423 (1150)	DTA, TGA, XRD		Martinez <i>et al.</i> ^[207]
	1373 (1100)	optimized		this work

CFM: cone fusion method; DSC: differential scanning calorimetry; ECM: electrical conductivity measurements; EDS: energy dispersive system; EMF: electromotive force; IM: isothermal method; SEM: scanning electron microscopy; VP: vacuum pyrolysis; other abbreviations see Tables I and II.

Solid solution was initially reported for α - and β -Ca₂P₂O₇ in the CaO-P₂O₅ system by Hill and al.^[91] but the careful XRD study performed by Kreidler and Hummel^[76] showed that dicalcium phosphate is stoichiometric.

5. Ca₄P₆O₁₉ (C₄P₃)

Hill *et al.*^[91] were the first to report the existence of this compound; they gave it the name trömelite in honor of Gerhard Trömel, who made the first systematic study of the CaO-P₂O₅ system. However, trömelite was never found in nature and for this reason it is not considered as a valid mineral name.^[24] According to Hill *et al.*'s^[91] quenching method, optical microscopy and XRD study, trömelite is a pentapolyphosphate (Ca₇P₁₀O₃₂; C₇P₅). This diagnostic was supported by paper chromatographic investigations made by Van Wazer and Ohashi^[95,96] who also identified the phase as a pentapolyphosphate. However, further chromatographic experiments by Wieker *et al.*^[97] showed that the phase is in fact a hexapolyphosphate of the likely composition Ca₄P₆O₁₉ (C₄P₃). This was later confirmed by a ³¹P NMR analysis performed by Gard.^[98]

No polymorphs are known for this compound. XRD data collected by Wieker *et al.*^[97] reveal that Ca₄P₆O₁₉ has a triclinic unit cell. The structure was refined

recently by Höpfe^[99] using XRD; according to him, Ca₄P₆O₁₉ crystallizes in the triclinic $P\bar{1}$ space group. For Hill *et al.*,^[91] Ca₄P₆O₁₉ melts incongruently to β -Ca₂P₂O₇ and liquid at 1258 K (985 °C). Recently, Szuszkiewicz^[100] determined the peritectic melting point by DTA and found 1273 K (1000 °C), which is in good agreement with Hill's data. Hill *et al.*^[91] reported some solid solution in trömelite and a lower limit of stability at 1168 K (895 °C). Kreidler and Hummel^[76] demonstrated by XRD that no such solid solution exists and that the phase is stable as low as 1073 K (800 °C). Szuszkiewicz^[100] confirmed the absence of solid solution and showed by DTA and XRD that Ca₄P₆O₁₉ is stable down to room temperature. All these data are summarized in Table V.

6. Ca(PO₃)₂ (CP)

This compound was first synthesized by Maddrell.^[101–103] It is known to exist in four polymorphic forms, α , β , γ , and δ . The highest temperature polymorph, α -Ca(PO₃)₂, was examined with an optical microscope by Schneiderhohn^[32]; he deduced that it fits the hexagonal system. A recent XRD and solid-state ³¹P NMR study made by Weil *et al.*^[104] rather shows that α -Ca(PO₃)₂ crystallizes in the monoclinic Cc space group. The intermediate temperature polymorph, β -Ca(PO₃)₂, was studied by Corbridge^[105] and Rothammel

Table IV. Melting and Polymorphic Transition Temperatures of Ca₂P₂O₇ (C₂P)

Transition	Temperature [K (°C)]	Technique	Comment	Reference	
Liq = α	1523 (1250)	TA		Nielsen ^[117]	
	1573 (1300)	OM, XRD		Trömel ^[36]	
	1573 (1300)	QM, OM, XRD		Barrett and McCaughey ^[38]	
	1626 (1353)	QM, OM, XRD		Hill <i>et al.</i> ^[91]	
	1623 (1350)	QM, XRD		Bale <i>et al.</i> ^[90]	
	1629 (1356)	QM, OM, XRD		St. Pierre ^[189]	
	1622 (1349)	TA		Stone <i>et al.</i> ^[222]	
	1623 (1350)	HM, TA		Trömel and Fix ^[40]	
	1628 (1355)	HM		Welch and Gutt ^[41]	
	1623 (1350)	TA, VPM		Urikh <i>et al.</i> ^[92]	
	1626 (1353)	DTA, XRD		Berak and Znamierowska ^[72,73,93]	
	1637 (1364)	DTA, XRD		Ismatov <i>et al.</i> ^[94]	
	1622 (1349)	optimized		this work	
	α ↔ β	1173 to 1473 (900 to 1200)	OM	crystals made by Trömel ^[36]	Schneiderhohn ^[32]
		1423 (1150)	OM, TA, XRD		Trömel ^[36]
		1393 (1120)	TA		Trömel ^[39]
1413 (1140)		QM, OM, XRD		Hill <i>et al.</i> ^[91]	
1543 (1270)		QM, XRD		Bale <i>et al.</i> ^[90]	
1393 (1120)		QM, TA, XRD		Trömel <i>et al.</i> ^[209]	
1423 (1150)		DTA, XRD		Ranby <i>et al.</i> ^[80]	
1413 (1140)		QM, XRD		McIntosh and Jablonski ^[87]	
1523 (1250)		DC		Egan Jr. and Wakefield ^[158]	
1493 (1220)		DTA, XRD		Mesmer and Irani ^[159]	
1444 to 1452 (1171 to 1179)		EPR, XRD	crystals doped with Mn ²⁺	Parodi <i>et al.</i> ^[88]	
1413 (1140)		DTA, XRD		Berak and Znamierowska ^[72,73,93]	
1438 (1165)		IM, XRD		Monma ^[223]	
1446 (1173)		DTA, XRD		Monma ^[223]	
1523 (1250)		TGA, XRD, IR, CA		Aoki ^[204]	
1413 (1140)		DTA, XRD		Jungowska ^[79]	
~1473 (~1200)		QM, TD, XRD		Bian <i>et al.</i> ^[224]	
1454 (1181)		DSC, TGA, XRD		Maciejewski <i>et al.</i> ^[120]	
1435 (1162)		DSC		Jacob <i>et al.</i> ^[160]	
β ↔ γ	1413 (1140)	optimized		this work	
	828 (555)	DTA		Fox and Clark ^[225]	
	873 to 973 (600 to 700)	not mentioned	probably QM, OM, XRD	Hill <i>et al.</i> ^[208]	
	1023 (750)	DTA, XRD		Ranby <i>et al.</i> ^[80]	
	973 to 1023 (700 to 750)	QM, XRD		McIntosh and Jablonski ^[87]	
	1123 (850)	DTA, XRD		Mesmer and Irani ^[159]	
	953 to 1013 (680 to 740)	EPR, XRD	crystals doped with Mn ²⁺	Parodi <i>et al.</i> ^[88]	
	900 (627)	DTA, XRD		Berak and Znamierowska ^[72,73,93]	
	1023 to 1473 (750 to 1200)	TGA, XRD, IR, CA		Aoki ^[204]	
	1074 (801)	DSC		Jacob <i>et al.</i> ^[160]	
	898 (625)	Optimized		this work	

DC: drop calorimetry; EPR: electron paramagnetic resonance; VPM: visual polythermal method; other abbreviations see Tables I through III.

and Burzlaff^[106] with XRD. Their investigations revealed that β-Ca(PO₃)₂ crystallizes in the monoclinic P2₁/c space group. A recent high temperature X-ray diffraction (HTXRD) study conducted by Viting *et al.*^[107] confirms the belonging to the monoclinic system. The next low temperature polymorph was first investigated by Boullé^[108] using XRD but no structure was derived. Hill *et al.*^[91] attributed the prefix γ to the phase examined by Boullé^[108] following an XRD study of various monocalcium phosphates. The structure of γ-Ca(PO₃)₂ was determined recently by Jackson *et al.*^[109] using XRD; it belongs to the monoclinic Cc space group. The lowest temperature polymorph in the series was first synthesized by Bale *et al.*^[90] and the prefix δ was later attributed to it by Hill *et al.*^[91]. Based on XRD data

collected by Bale *et al.*,^[110] δ-Ca(PO₃)₂ crystallizes in the tetragonal system.

The melting point of α-Ca(PO₃)₂ is congruent and lies only between 1233 and 1293 K (960 and 1020 °C), which is rather small. The same is true for the α-β transition where the observed temperatures range between 1200 K and 1251 K (927 °C and 978 °C). For the β-γ transition, the temperatures mentioned in the literature vary between 673 K and 993 K (400 and 720 °C; Table V). The highest temperatures [963 K to 993 K (690 °C to 720 °C)] were reported by Jackson *et al.*^[109] using DSC, TGA and XRD. We discarded their data because they measured at 963 K to 993 K (690 °C to 720 °C) an enthalpy of transition of 24 ± 1 kJ mol⁻¹, an unreasonable large value for such a polymorphic transformation. The

Table V. Melting and Polymorphic Transition Temperatures of $\text{Ca}_4\text{P}_6\text{O}_{19}$ (C_4P_3), $\text{Ca}_2\text{P}_6\text{O}_{17}$ (C_2P_3), and $\text{CaP}_4\text{O}_{11}$ (CP_2)

Compound	Transition	Temperature [K (°C)]	Technique	Comment	Reference
$\text{Ca}_4\text{P}_6\text{O}_{19}$	$\beta\text{-C}_2\text{P} + \text{Liq} = \text{C}_4\text{P}_3$	1258 (985)	QM, OM, XRD	unstable below 1188 K (915 °C)	Hill <i>et al.</i> ^[91]
		1273 (1000)	DTA, XRD		Szuskiewicz ^[100]
		1242 (969)	optimized		this work
$\text{Ca}_2\text{P}_6\text{O}_{17}$	$\beta\text{-CP} + \text{Liq} = \text{C}_2\text{P}_3$	1047 (774)	QM, OM, XRD	no indication on type of melting peritectoid: $\text{C}_2\text{P}_3 = \gamma\text{-CP} + \alpha\text{-CP}_2$	Hill <i>et al.</i> ^[91]
		1053 (780)	DTA, TGA		Meyer <i>et al.</i> ^[112]
		668 (395)	inferred from study of CP_2 phase		Viting <i>et al.</i> ^[107]
$\text{CaP}_4\text{O}_{11}$	$\text{Liq} = \alpha$	1040 (767)	optimized	peritectoid: $\alpha\text{-CP}_2 = \gamma\text{-CP} + \text{O-P}_2\text{O}_5$	this work
		1083 (810)	QM, OM, XRD		Hill <i>et al.</i> ^[91]
		1063 (790)	QM, DTA, XRD		Beucher ^[114]
		1063 (790)	DTA		Churakova <i>et al.</i> ^[116]
		1063 (790)	DTA, HTXRD		Lazoryak <i>et al.</i> ^[226]
		1083 (810)	DTA, TGA		Meyer <i>et al.</i> ^[112]
		673 (400)	HTXRD		Viting <i>et al.</i> ^[107]
		1046 (773)	optimized		this work
		613 (340)	DTA		Churakova <i>et al.</i> ^[116]
		358 (85)	HTXRD		Schneider ^[113]
$\alpha \leftrightarrow \beta$	$\alpha \leftrightarrow \beta$	613 (340)	HTXRD	in air in nitrogen in air	Viting <i>et al.</i> ^[107]
		613(340)	optimized		this work

Abbreviations: see Tables I and II.

remaining data range mostly between 773 K and 823 K (500 °C and 550 °C) and our preference went to them. The temperature of the $\gamma\text{-}\delta$ transformation is not known; for this reason, and due to the fact that no thermodynamic information is known for $\delta\text{-Ca}(\text{PO}_3)_2$, the polymorph is not considered in the present study.

Some solid solution was initially reported for the α - and $\beta\text{-Ca}(\text{PO}_3)_2$ phases by Hill *et al.*^[91] but the careful XRD study performed by Kreidler and Hummel^[76] demonstrated that $\text{Ca}(\text{PO}_3)_2$ is stoichiometric.

7. $\text{Ca}_2\text{P}_6\text{O}_{17}$ (C_2P_3)

No polymorphs are known for this compound. According to Stachel^[111] and Meyer *et al.*^[112] who used XRD, $\text{Ca}_2\text{P}_6\text{O}_{17}$ crystallizes in the monoclinic $P2_1/c$ space group. Hill *et al.*^[91] employed the quenching technique, optical microscope, and XRD and found that $\text{Ca}_2\text{P}_6\text{O}_{17}$ melts incongruently to $\beta\text{-CaP}_2\text{O}_6$ and liquid at 1047 K (774 °C). Using DTA, Meyer *et al.*^[112] obtained 1053 K (780 °C) but did not specify if the melting was congruent or not. The only discordant data is from Viting *et al.*^[107] who observed by HTXRD that $\alpha\text{-CaP}_4\text{O}_{11}$ (CP_2 , see next compound below) decomposes very slowly to $\gamma\text{-Ca}(\text{PO}_3)_2$ ($\gamma\text{-CP}$) and P_2O_5 above about 673 K (400 °C). Consequently, $\text{Ca}_2\text{P}_6\text{O}_{17}$ (C_2P_3) could only be stable up to about 668 K (395 °C) where it would decompose to $\gamma\text{-CaP}_2\text{O}_6$ ($\gamma\text{-CP}$) and P_2O_5 . This data was not considered because quenching experiments performed by Hill *et al.*^[91] in the $\text{CaO-P}_2\text{O}_5$ binary show that starting materials containing more than 0.612 mol fraction P_2O_5 cannot remain homogeneous in open crucibles due to P_2O_5 loss by volatilization. Samples investigated by Viting *et al.*^[107] were typically subjected to 1 to 5 hours (and even longer) thermal treatments in air, which may have resulted in excessive P_2O_5 loss and produced the discordant results reported by them. The data are summarized in Table V.

8. $\text{CaP}_4\text{O}_{11}$ (CP_2)

The compound $\text{CaP}_4\text{O}_{11}$ exists in two polymorphic forms, α and β . The high temperature polymorph, $\alpha\text{-CaP}_4\text{O}_{11}$, was studied by Schneider *et al.*^[113] using XRD; it was found to crystallize in the orthorhombic $Aea2$ space group. The belonging to the orthorhombic system was recently confirmed by a high temperature XRD investigation made by Viting *et al.*^[107] According to the XRD studies of Meyer *et al.*^[112] Schneider *et al.*^[113] Beucher,^[114] and Tordjman *et al.*^[115] the low temperature polymorph, $\beta\text{-CaP}_4\text{O}_{11}$, crystallizes in the monoclinic space group $P2_1/c$. In his high temperature XRD investigation, Viting *et al.*^[107] concluded as well that $\alpha\text{-CaP}_4\text{O}_{11}$ is monoclinic.

Melting temperatures reported in the literature (Table V) for $\alpha\text{-CaP}_4\text{O}_{11}$ are in very good agreement with each other; they lie between 1063 K and 1083 K (790 °C and 810 °C). The only data at odd with these are from Viting *et al.*^[107] As explained above for the C_2P_3 phase, the high-temperature XRD study of Viting *et al.*^[107] shows that $\alpha\text{-CaP}_4\text{O}_{11}$ decomposes very slowly in air to $\gamma\text{-Ca}(\text{PO}_3)_2$ and P_2O_5 above 673 K (400 °C); this data was not used because P_2O_5 loss probably occurred during their experiments.

The polymorphic transition between α - and $\beta\text{-CaP}_4\text{O}_{11}$ was first detected by Churakova *et al.*^[116] who observed a weak endothermic effect at 613 K

Table VI. Melting and Polymorphic Transition Temperatures of Ca(PO₃)₂ (CP)

Transition	Temperature [K (°C)]	Technique	Comment	Reference	
Liq = α	1293 (1020)	TA		Nielsen ^[117]	
	1248 (975)	OM, TA, XRD		Trömel ^[36]	
	1283 (1010)	QM, DTA, XRD		Boullé ^[108,227]	
	1253 (980)	QM, OM, XRD		Barrett and McCaughey ^[38]	
	1257 (984)	QM, OM, XRD		Hill <i>et al.</i> ^[91]	
	1273 (1000)	QM, XRD		Bale <i>et al.</i> ^[90]	
	1252 (979)	QM, OM		Stone <i>et al.</i> ^[222]	
	1233 (965)	QM, PC, XRD		Thilo and Grunze ^[228]	
	1242 (969)	DTA, OM		Sokolova ^[229]	
	1249 (976)	DTA, XRD		Andrieux and Diament ^[230]	
	1243 (970)	DTA, IR, XRD		Bekturov <i>et al.</i> ^[231]	
	1237 (964)	DTA		Henry and Durif ^[232]	
	1238 (965)	DTA		Grenier <i>et al.</i> ^[233]	
	1241 (968)	DTA		Henry and Durif ^[234, 235]	
	1241 (968)	DTA		Rakotomahanina-Rolaisoa ^[236]	
	1249 (976)	DTA	DTA heating curve	Serazetdinv <i>et al.</i> ^[237]	
	1243 (970)	DTA	DTA cooling curve	Serazetdinv <i>et al.</i> ^[237]	
	1251 (978)	DTA		Tokman and Bukhalova, ^[238] Bukhalova <i>et al.</i> ^[239]	
	1243 (970)	TA	melting observed directly	Urikh <i>et al.</i> ^[92]	
	1238 (965)	DTA, XRD		Hattori <i>et al.</i> ^[240]	
	1253 (980)	DTA, PC, IR, XRD		Kuźmenkov <i>et al.</i> ^[241]	
1293 (1020)	DTA, XRD		Bukhalova <i>et al.</i> ^[242]		
1257 (984)	DTA, OM, IR, XRD		Szuskiewicz ^[243]		
1273 (1000)	TGA, XRD, IR, CA		Aoki ^[204]		
1243 (970)	DTA, TGA		Meyer <i>et al.</i> ^[112]		
1251 (978)	Optimized		this work		
α ↔ β	1236 (963)	QM, OM, XRD		Hill <i>et al.</i> ^[91]	
	1243 (970)	QM, XRD		McIntosch and Jablonski ^[87]	
	1200 (927)	DTA		Henry and Durif ^[232]	
	1213 (940)	DTA		Grenier <i>et al.</i> ^[233]	
	1201 (928)	DTA		Henry and Durif ^[234]	
	1200 (927)	DTA		Henry and Durif ^[235]	
	1232 (959)	DTA		Rakotomahanina-Rolaisoa ^[236]	
	1237 (964)	DTA, OM, IR, XRD		Szuskiewicz ^[243]	
	1251 (978)	DTA, XRD		Vassel <i>et al.</i> ^[244]	
	1223 to 1243 (950 to 970)	TGA, XRD, IR, CA		Aoki ^[204]	
	1246 (973)	optimized		this work	
	β ↔ γ	673 (400)	QM, DTA, XRD		Boullé ^[108,227]
		723 to 773 (450 to 500)	QM, XRD		McIntosch and Jablonski ^[87]
723 to 773 (450 to 500)		PC, OM, TGA, XRD		Morrin ^[245]	
773 to 873 (500 to 600)		DTA, IR, XRD		Bekturov <i>et al.</i> ^[231]	
813 to 913 (540 to 640)		TGA, XRD, IR, CA		Aoki ^[204]	
>773 (>500)		HTXRD		Viting <i>et al.</i> ^[107]	
963 to 993 (690 to 720)		DSC, TGA, XRD		Jackson <i>et al.</i> ^[109]	
773 (500)		optimized		this work	

PC: paper chromatography; other abbreviations see Tables I through III.

(340 °C) on a DTA profile collected with CaP₄O₁₁. This effect was also seen at 613 K (340 °C) by Viting *et al.*^[107] using high temperature XRD and was interpreted as a polymorphic transition. Using the same technique, Schneider *et al.*^[113] located the same transformation at 358 K (85 °C) in nitrogen. Results reported by Churakova *et al.*^[116] and Viting *et al.*^[107] at 613 K (340 °C) were selected because they were performed in air.

B. Liquidus and Solidus Phase Diagram Data

In addition to the melting and polymorphic transition data listed in Tables II through VI, numerous phase equilibrium data, such as liquidus and solidus data, are

also available. These data were obtained by Nielsen^[117] using thermal analysis between 0.250 and 0.500 mol fraction P₂O₅, by Trömel^[36] using thermal analysis, optical microscopy, and XRD between 0.161 and 0.53 mol fraction P₂O₅, by Behrendt and Wentrup^[37] using thermal analysis between 0.119 and 0.245 mol fraction P₂O₅, by Frear *et al.*^[118] using the quenching method and optical microscopy between 0.291 and 0.323 mol fraction P₂O₅, by Barrett and McCaughey^[38] using oxy-acetylene flame, pyrometer, quenching method, optical microscopy, and XRD between about 0.20 and 0.30 mol fraction P₂O₅ (note that they only measured the temperatures of some peritectic and eutectic points; the compositions of the points were not determined), by

Table VII. Invariant Reaction Points Involving the Liquidus of the CaO-P₂O₅ System

Type of Invariant Reaction	Reaction	Temperature [K (°C)]	Composition (Mole fr. P ₂ O ₅)	Technique	Reference
Peritectic	CaO + Liq = α-C ₄ P	1943 (1670)		QM, OM, XRD	Barrett and McCaughey ^[38]
		1913 (1640)	-0.209	TA	Trömel ^[39]
		1983 ± 20 (1710 ± 20)	-0.206	HM	Trömel and Fix ^[40]
		1993 (1720)	-0.209	HM	Welch and Gutt ^[41]
		2021 (1748)	0.200	optimized	this work
Eutectic	Liq = α-C ₄ P + α-C ₃ P	1833 (1560)	0.230	TA, OM, XRD	Trömel ^[36]
		1843 (1570)		QM, OM, XRD	Barrett and McCaughey ^[38]
		1853 ± 10 (1580 ± 10)	-0.233	TA	Trömel and Fix ^[40]
		1853 (1580)	-0.233	HM	Welch and Gutt ^[41]
		1887 (1614)	0.237	optimized	this work
Eutectic	Liq = α-C ₃ P + α-C ₂ P	1558 (1285)	0.308	TA, OM, XRD	Trömel ^[36]
		1553 (1280)		QM, OM, XRD	Barrett and McCaughey ^[38]
		1567 (1294)	-0.300	QM, OM	Frear <i>et al.</i> ^[118]
		1563 ± 10 (1290 ± 10)	-0.296	TA	Trömel and Fix ^[40]
		1560 (1287)	-0.302	HM	Welch and Gutt ^[41]
		1559 (1286)	0.300	TA, OM, XRD	Berak and Znamierowska ^[73]
		1557 ± 5 (1284 ± 5)	0.301	DSC, TGA, XRD	Maciejewski <i>et al.</i> ^[120]
		1569 (1296)	0.289	optimized	this work
		1258 ± 1 (985 ± 1)	0.471	QM, OM, XRD	Hill <i>et al.</i> ^[91]
Peritectic	β-C ₂ P + Liq = C ₄ P ₃	1273 (1000)	-0.434	DTA, XRD	Szuskiewicz ^[100]
		1242 (969)	0.465	optimized	this work
		1243 (970)	0.456	TA, OM, XRD	Trömel ^[36]
Eutectic	Liq = C ₄ P ₃ + α-CP	1243 ± 1 (970 ± 1)	0.476 ± 0.3	QM, OM, XRD	Hill <i>et al.</i> ^[91]
		1242 (969)	0.469	optimized	this work
Peritectic	β-CP + Liq = C ₂ P ₃	1047 ± 2 (774 ± 2)	0.605 ± 0.6	QM, OM, XRD	Hill <i>et al.</i> ^[91]
		1053 (780)		DTA, TGA	Meyer <i>et al.</i> ^[112]
		1040 (767)	0.627	optimized	this work
Eutectic	Liq = C ₂ P ₃ + α-CP ₂	1019 ± 5 (746 ± 5)	0.629 ± 1.3	QM, OM, XRD	Hill <i>et al.</i> ^[91]
		1034 (761)	0.634	optimized	this work
Eutectic	Liq = α-CP ₂ + O'-P ₂ O ₅	763 ± 5 (490 ± 5)	0.855 ± 1.3	QM, OM, XRD	Hill <i>et al.</i> ^[91]
		738 (465)	0.847	optimized	this work

Abbreviations: see Tables I through III.

Hill *et al.*^[91] using the quenching method, optical microscopy, and XRD between 0.334 and 0.949 mol fraction P₂O₅, by Trömel and Fix^[40] using the quenching method, heating microscopy, thermal analysis, and XRD between 0.195 and 0.334 mol fraction P₂O₅, by Welch and Gutt^[41] using heating microscopy between 0.20 and 0.334 mol fraction P₂O₅, by Trömel and Fix^[119] using the quenching method and optical microscopy between 0.202 and 0.209 mol fraction P₂O₅, by Berak and Znamierowska^[73] using thermal analysis, optical microscopy, and XRD between 0.25 and 0.335 mol fraction P₂O₅, and by Maciejewski *et al.*^[120] using DSC, TGA, and XRD between 0.248 and 0.333 mol fraction P₂O₅. All these data are in general in good agreement with each other. The only data discarded are the ones collected by Welch and Gutt^[41] along the liquidus. According to the XRD study of Kreidler and Hummel,^[76] P₂O₅ lost probably occurred during Welch and Gutt's experiments, which make their results unreliable. Invariant points involving the liquidus are reported in Table VII.

C. Thermodynamic Data

Thermodynamic properties of end-members are listed in Table VIII. All available enthalpy, entropy, and heat

capacity data are summarized in Tables IX through XII. Details about data selection are given below for each compound and experimental data are depicted in Figures 2 through 7. As far as we know, no thermodynamic data are available for Ca₁₀(PO₄)₆O₂ (C₁₀P₃), Ca₄P₆O₁₉ (C₄P₃), and Ca₂P₆O₁₇ (C₂P₃).

1. CaO and P₂O₅

Thermodynamic data for the end-members CaO and P₂O₅ were taken from previous optimizations that can be found in FactSage FToxide database (Bale *et al.*^[121]) and Jung and Hudon,^[19] respectively. The data are listed in Table VIII.

2. Ca₄(PO₄)₂O (C₄P)

Martin *et al.*^[122] used isothermal calorimetry to measure the standard heat of formation of α-Ca₄(PO₄)₂O at 310.55 (37.4 °C) and obtained -717.072 kJ mol⁻¹ from the oxides. The heat content $H_T - H_{298.15K}^0$ of α-Ca₄(PO₄)₂O (Figure 2) was determined between 679 K and 1611 K (406 °C and 1338 °C) using adiabatic calorimetry and an equation for the heat capacity was derived from the measurements by Sokolov *et al.*^[123] The only thermodynamic data available for β-Ca₄(PO₄)₂O is the standard heat of formation which was measured by Jeffes

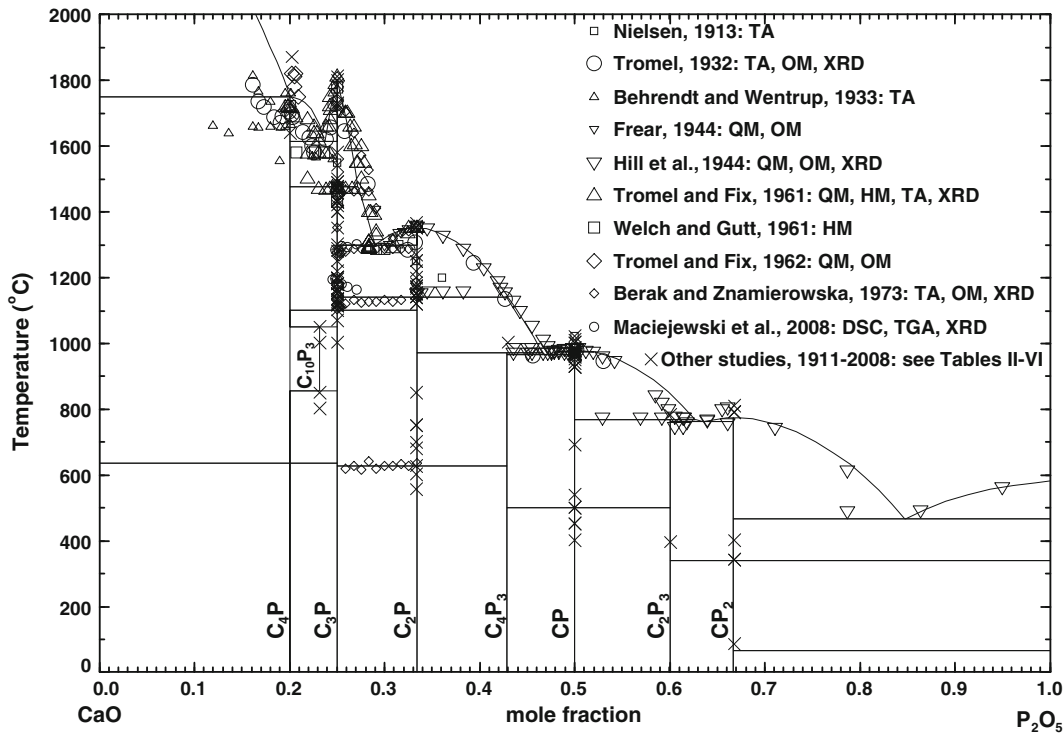


Fig. 1—The binary CaO-P₂O₅ system along with experimental data of Nielsen,^[117] Trömel,^[36] Behrendt and Wentrup,^[37] Frear,^[118] Hill *et al.*,^[91] Trömel and Fix,^[40] Welch and Gutt,^[41] Trömel and Fix,^[119] Berak and Znamierowska,^[73] Maciejewski *et al.*,^[120] and other studies (1911 to 2008) from Tables 2 through 6. Abbreviations are the same as the ones listed in the tables.

Table VIII. Thermodynamic Properties of the End-Members CaO and P₂O₅

End-Member	Property	Reference
CaO (l)	$\Delta H_f^{\circ}_{298.15\text{ K}} = -555.594\text{ kJ mol}^{-1}$; $S_{298.15\text{ K}}^{\circ} = 65.691\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [298.15\text{ K to } 2845\text{ K}] = 58.79117057$ $- 1,147,145.982T^{-2} - 133.9039996T^{0.5} + 102,978,787.86T^{-3}\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [>2845\text{ K (2572 }^{\circ}\text{C)}] = 62.760\text{ J mol}^{-1}\text{ K}^{-1}$	Bale <i>et al.</i> ^[121]
CaO (s)	$\Delta H_f^{\circ}_{298.15\text{ K}} = -635.090\text{ kJ mol}^{-1}$; $S_{298.15\text{ K}}^{\circ} = 37.750\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [298.15\text{ K to } 853\text{ K}] = 58.79117057$ $- 1,147,145.982T^{-2} - 133.9039996T^{0.5} + 102,978,787.86T^{-3}\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [>2845\text{ K}] = 62.760\text{ J mol}^{-1}\text{ K}^{-1}$	Bale <i>et al.</i> ^[121]
P ₂ O ₅ (l)	$\Delta H_f^{\circ}_{298.15\text{ K}} = -1512.358\text{ kJ mol}^{-1}$; $S_{298.15\text{ K}}^{\circ} = 124.000\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [298.15\text{ K to } 853\text{ K}] = -21.643407 + 0.3362284T$ $- 3516373T^{-2} + 0.000112629T^2 + 22,900.402T^{-1}\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [>853\text{ K}] = 225.000\text{ J mol}^{-1}\text{ K}^{-1}$	Jung and Hudon ^[19]
O'-P ₂ O ₅ (s)	$\Delta H_f^{\circ}_{298.15\text{ K}} = -1539.013\text{ kJ mol}^{-1}$; $S_{298.15\text{ K}}^{\circ} = 91.600\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [298.15\text{ K to } 1000\text{ K}] = -21.643407 + 0.3362284T$ $- 3516373T^{-2} + 0.000112629T^2 + 22,900.402T^{-1}\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [>1000\text{ K}] = 225.000\text{ J mol}^{-1}\text{ K}^{-1}$	Jung and Hudon ^[19]
O-P ₂ O ₅ (s)	$\Delta H_f^{\circ}_{298.15\text{ K}} = -1539.402\text{ kJ mol}^{-1}$; $S_{298.15\text{ K}}^{\circ} = 92.750\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [298.15\text{ K to } 1000\text{ K}] = -21.643407 + 0.3362284T$ $- 3516373T^{-2} + 0.000112629T^2 + 22,900.402T^{-1}\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [>1000\text{ K}] = 225.000\text{ J mol}^{-1}\text{ K}^{-1}$	Jung and Hudon ^[19]
H-P ₂ O ₅ (s)	$\Delta H_f^{\circ}_{298.15\text{ K}} = -1504.968\text{ kJ mol}^{-1}$; $S_{298.15\text{ K}}^{\circ} = 114.391\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [298.15\text{ K to } 1000\text{ K}] = -21.643407$ $+ 0.3362284T - 3516373T^{-2} + 0.000112629T^2 + 22,900.402T^{-1}\text{ J mol}^{-1}\text{ K}^{-1}$ $C_p [>1000\text{ K}] = 225.000\text{ J mol}^{-1}\text{ K}^{-1}$	Jung and Hudon ^[19]

(unpublished result cited in Pearson *et al.*^{[124])} using hydrochloric acid solution calorimetry. He found $-723.455\text{ kJ mol}^{-1}$ at 348 K (75 °C) from the oxides.

The standard Gibbs energy of formation of Ca₄(PO₄)₂O was first measured by Bookey *et al.*^[125] from

the reaction $2P_{\text{in Fe}} + 5O_{\text{in Fe}} + 4\text{CaO(s)} = \text{Ca}_4(\text{PO}_4)_2\text{O(s)}$ between 1833 K and 1873 K (1560 °C and 1600 °C). Liquid iron, containing phosphorus and oxygen, was equilibrated with a mixture of solid CaO and Ca₄(PO₄)₂O (in a crucible made of CaO and

Table IX. Standard Enthalpies of Formation of Compounds in the CaO-P₂O₅ System Optimized in the Present Study and Compared with Experimental Data (reference state of P₂O₅ is hexagonal P₂O₅)

Phase	ΔH_f° 298.15 K (kJ mol ⁻¹) Elements as Reference	ΔH_f° 298.15 K (kJ mol ⁻¹) Solid Oxide as Reference	Technique	Reference/ Comment
α -Ca ₄ (PO ₄) ₂ O	-4762.400 ± 10 at 310 K (37 °C) -4751.500	-717.072 at 310 K (37 °C) -706.172	IC	Martin <i>et al.</i> ^[122] this work
β -Ca ₄ (PO ₄) ₂ O	-4768.783 at 348 K (75 °C) -4766.500	-723.455 at 348 K (75 °C) -721.172	HCl-SC optimized	Jeffes in Pearson <i>et al.</i> ^[124] this work
Ca ₁₀ (PO ₄) ₆ O ₂	-1294.566834	-2079.864	optimized	this work
α' -Ca ₃ (PO ₄) ₂	-3859.740 ± 25.1 -4068.579	-449.502 -658.341	KEM	Butylin <i>et al.</i> ^[140] , estimated from 1750 K (1477 °C); doubtful this work
α -Ca ₃ (PO ₄) ₂	-4091.952 -4096.500 ± 10 at 310 K (37 °C) -4057.761	-681.714 -686.262 at 310 K (37 °C) -647.523	HCl-SC IC	Smirnova <i>et al.</i> ^[142] Martin <i>et al.</i> ^[122] this work
β -Ca ₃ (PO ₄) ₂	-4097.81 ± 4.2 -4096.414	-687.572 -686.176	IC	Berthelot ^[146-148] recalculated by Smirnova <i>et al.</i> ^[142] Richardson <i>et al.</i> ^[130] using data of Matignon and Séon ^[149]
	-4090.891 at 348 K (75 °C) -4112.872	-680.653 at 348 K (75 °C) -702.634	HCl-SC HCl-SC	Jeffes in Pearson <i>et al.</i> ^[124] Smirnova <i>et al.</i> ^[142]
	-4116.497 at 308 K (35 °C) -4128.192	-706.259 ± 8.4 at 308 K (35 °C) -717.954 ± 16.7	HCl-SC SC	Meadowcroft and Richardson ^[151] Jacques <i>et al.</i> in Meadowcroft and Richardson ^[151]
α -Ca ₂ P ₂ O ₇	-4056.000 -4097.545	-645.762 -687.307	HNO ₃ -SC optimized	Ben Abdelkader <i>et al.</i> ^[152] this work
	-3301.176 ± 54.4 -3343.000 ± 6 -3324.000 ± 8	-526.028 -567.852 -548.852	KEM KEM KEM	Butylin <i>et al.</i> ^[140] , estimated from 1555 K (1282 °C) Lopatin ^[156] , estimated from 1409 K to 1560 K (1136 °C to 1287 °C) Lopatin ^[156] recalculated by Lopatin ^[157] Egan and Wakefield ^[165]
β -Ca ₂ P ₂ O ₇	-3314.811 -3321.506	-539.663 -546.358	optimized optimized	this work this work
γ -Ca ₂ P ₂ O ₇	-3346.264 at 308 K (35 °C) -3321.778	-571.116 ± 7.5 at 308 K (35 °C) -546.630	HCl-SC optimized	Meadowcroft and Richardson ^[151] this work
Ca ₄ P ₆ O ₁₉	-8275.093	-1219.829	optimized	this work
α -Ca(PO ₃) ₂	-2472.878	-332.820	optimized	this work
β -Ca(PO ₃) ₂	-2476.928 ± 29.3	-336.870	KEM	Butylin <i>et al.</i> , ^[140] Rat'kovskii <i>et al.</i> ^[163] , estimated from 1100 K and 1180 K (827 °C and 907 °C)
	-2456.008 ± 10.5 -2483.000 ± 7 -2470.000 ± 5	-315.950 -342.942 -329.942	KEM KEM KEM	Rat'kovskii <i>et al.</i> ^[164] , estimated from 1080 K (807 °C) Lopatin ^[156] , estimated from 1132 K to 1215 K (859 °C to 942 °C) Lopatin ^[156] recalculated by Lopatin ^[157]
γ -Ca(PO ₃) ₂	-2474.878 -2480.694 ± 11.7 -2476.878	-334.820 -340.636 -336.820	optimized DTA optimized	this work Volkov <i>et al.</i> ^[167] this work
Ca ₂ P ₆ O ₁₇	-6526.624	-741.540	optimized	this work
α -CaP ₄ O ₁₁	-4045.648	-400.622	optimized	this work
β -CaP ₄ O ₁₁	-4038.000 ± 21	-392.974	KEM	Golubchenko ^[168] , estimated from 808 K to 923 K (535 °C to 650 °C) and recalculated by Lopatin ^[157]
	-4048.148	-403.122	optimized	this work

HCl-SC: hydrochloric acid solution calorimetry; HNO₃-SC: nitric acid solution calorimetry; KEM: Knudsen effusion method; IC: isothermal calorimetry; SC: solution calorimetry; other abbreviations see Tables II through IV.

Table X. Melting and transition enthalpies of compounds in the CaO-P₂O₅ system optimized in the present study and compared with experimental data

Phase	$\Delta H_{\text{fus}}^{\circ}$ (solid \rightarrow liquid) (kJ mol ⁻¹)	$\Delta H_{\text{tr}}^{\circ}$ (low- $T \rightarrow$ high- T) (kJ mol ⁻¹)	Technique	Reference/ Comment
α -Ca ₄ (PO ₄) ₂ O	-113.320 at 2021 K (1748 °C)		optimized	this work
β -Ca ₄ (PO ₄) ₂ O		15.000 at 908 K (635 °C)	optimized	this work
α' -Ca ₃ (PO ₄) ₂	-31.530 at 2076 K (1803 °C)		optimized	this work
α -Ca ₃ (PO ₄) ₂		73.220 \pm 12.6 at 1748 K (1475 °C)	CCR	Riboud ^[141] ; doubtful
		20.650 at 1748 K (1475 °C)	Optimized	this work
β -Ca ₃ (PO ₄) ₂		18.828 at 1373 K (1100 °C)	SC	Britzke and Veselovskii ^[144]
		21.644 at 1398 K (1125 °C)	optimized	this work
α -Ca ₂ P ₂ O ₇	-100.851 at 1626 K (1353 °C)		DC	Egan and Wakefield ^[158]
	-86.650 at 1624 K (1351 °C)		optimized	this work
β -Ca ₂ P ₂ O ₇		6.786 at 1413 K (1140 °C)	DC	Egan and Wakefield ^[158]
		6.360 at 1493 K (1220 °C)	DTA	Mesmer and Irani ^[159]
		6.551 \pm 0.7 at 1435 K (1162 °C)	DSC	Jakob <i>et al.</i> ^[160]
		6.694 at 1433 K (1160 °C)	optimized	this work
γ -Ca ₂ P ₂ O ₇		1.674 at 1123 K (850 °C)	DTA	Mesmer and Irani ^[159]
		1.074 \pm 0.2 at 1074 K (801 °C)	DSC	Jakob <i>et al.</i> ^[160]
		0.272 at 898 K (625 °C)	optimized	this work
Ca ₄ P ₆ O ₁₉	-154.400 at 1244 K (971 °C)		optimized	this work
α -Ca(PO ₃) ₂	-64.720 at 1251 K (978 °C)		optimized	this work
β -Ca(PO ₃) ₂		2.000 at 1246 K (973 °C)	optimized	this work
γ -Ca(PO ₃) ₂		24 \pm 1 at 963 K (690 °C)	DSC	Jackson <i>et al.</i> ^[109] ; doubtful
		2.000 at 773 K (500 °C)	optimized	this work
Ca ₂ P ₆ O ₁₇	-100.910 at 1038 K (765 °C)		optimized	this work
α -CaP ₄ O ₁₁	-75.550 at 1044 K (771 °C)		optimized	this work
β -CaP ₄ O ₁₁		2.500 at 613 K (340 °C)	optimized	this work

CCR: Clausius–Clapeyron relation; other abbreviations see Tables II through IX.

Ca₄(PO₄)₂O under an oxygen partial pressure controlled by H₂ and H₂O. The Gibbs energy of formation of Ca₄(PO₄)₂O was also determined by Bookey^[126] using the reaction 4Ca₄(PO₄)₂O(s) + 5H₂(g) = 4CaO(s) + P₂(g) + 5H₂O(g) between 1523 K and 1773 K (1250 °C and 1500 °C). Measurements consisted of passing a known volume of hydrogen over C₃P(s), contained in a molybdenum boat within an impervious alumina tube, and the determination of the amount of H₂O(g) in the exit gas. Although a certain amount of Mo₃P was formed during the experiment, this had no effect on the determination of the Gibbs energy of the reaction above. Ban-Ya and Matoba^[127] determined the Gibbs energy of formation of Ca₄(PO₄)₂O from the reactions 4CaO(s) + 2P_{in Fe} + 5CO₂(g) = Ca₄(PO₄)₂O(s) + 5CO(g) and 4CaO(s) + 2P_{in Fe} + 5CO(g) = Ca₄(PO₄)₂O(s) + 5C_{in Fe} between 1803 K and 1858 K (1530 °C and 1585 °C). Fe-C-P melts were equilibrated with solid CaO and Ca₄(PO₄)₂O in CaO or Ca₄(PO₄)₂O crucibles under a controlled CO-CO₂ gas mix. Aratani *et al.*^[128] determined the Gibbs energy of formation from the reactions 4CaO(s) + 2P_{in Fe} + 5H₂O(g) = Ca₄(PO₄)₂O + 5H₂(g) and H₂(g) + O_{in Fe} = H₂O(g) between 1813 K and 1873 K (1540 °C and 1600 °C). Iron melts containing phosphorus were equilibrated in CaO crucibles under a controlled H₂-H₂O atmosphere. Iwase *et al.*^[129,130] employed two techniques to determine the Gibbs energy of formation. First, they measured the emf of the electrochemical cell Mo/Mo + MoO₂//ZrO₂(MgO)//(Cu + P)_{alloy} + (CaO + CaCl₂ + P₂O₅)_{slag} + CaO + Ca₄(PO₄)₂O/Mo between 1423 K and 1523 K (1150 °C and 1250 °C) and second, they equilibrated the reaction

4CaO(s) + 2P_{in Cu} + 5CO(g) = 4Ca₄(PO₄)₂O(s) + 5C(s) at 1473 K (1200 °C. In this last experiment, molten copper was brought to equilibrium with solid CaO and Ca₄(PO₄)₂O in a graphite crucible under a stream of CO gas. Both techniques gave consistent results. Tagaya *et al.*^[131,132] measured the Gibbs energy of formation between 1473 K and 1598 K (1200 °C and 1325 °C) using the reactions 3Ca₄(PO₄)₂O(s) + 2P_{in Ag} + 5CO(g) = 4Ca₃(PO₄)₂(s) + 5C(s) and Ca₃(PO₄)₂(s) + Ca_{in Ag} + CO(g) = Ca₄(PO₄)₂O(s). Mixtures of Ca₃(PO₄)₂(s) and Ca₄(PO₄)₂O(s) were equilibrated with silver-phosphorus alloys in graphite crucibles under CO and Ar mixtures. The Gibbs energy of formation of Ca₄(PO₄)₂O(s) was also measured by Nagai *et al.*^[133] between 1523 K and 1623 K (1250 °C and 1350 °C) using double Knudsen cell mass spectrometry. Recently, Yamasue *et al.*^[134] determined the Gibbs energy of formation from the reaction Ca₄(PO₄)₂O(s) + 5C(s) = 4CaO(s) + P₂(g) + 5CO(g) between 1373 K and 1573 K (1100 °C and 1300 °C). Measurements consisted of passing a known volume of Ar-CO gas over C₄P(s), contained in a graphite chamber, and the determination of the amount of P₂(g) in the exit gas. All the Gibbs energies of the reactions obtained experimentally were converted to 4Ca(l) + P₂(g) + 4.5O₂(g) = Ca₄(PO₄)₂O(s) using Gibbs energy of the reactions Ca(l) + O₂(g) = CaO(s) from FactSage (Bale *et al.*^[121]), 2.5O₂(g) = 5O_{in Fe} from Sakao and Sano^[135] and Elliot and Gleiser,^[136] P₂(g) = 2P_{in Fe} from Yamamoto *et al.*^[137], and 0.5P₂(g) = P_{in Ag} from Ban-Ya and Suzuki^[138] and Yamamoto *et al.*^[139] The resultant Gibbs energy of formation of Ca₄(PO₄)₂O from all the experiments are depicted in Figure 6(a).

Table XI. Standard Entropies of Formation of Compounds in the CaO-P₂O₅ System Optimized in the Present Study and Compared with Experimental Data (reference state of P₂O₅ is hexagonal P₂O₅)

Phase	$S_{298.15\text{K}}^{\circ}$ (J mol ⁻¹ K ⁻¹) Elements as reference	$\Delta S_{298.15\text{K}}^{\circ}$ (J mol ⁻¹ K ⁻¹) Solid Oxides as Reference	Technique	Comment	Reference
α -Ca ₄ (PO ₄) ₂ O	270.000	4.610	optimized		this work
β -Ca ₄ (PO ₄) ₂ O	253.490	-11.900	optimized		this work
Ca ₁₀ (PO ₄) ₆ O ₂	743.367	22.696	optimized		this work
α' -Ca ₃ (PO ₄) ₂	233.886 ± 13.0	6.246	KEM		Butylin <i>et al.</i> ^[140] ; doubtful
	214.134	-13.506	optimized		this work
α -Ca ₃ (PO ₄) ₂	240.915	13.275	AC		Southard and Milner ^[143]
	240.703	13.063	optimized		this work
β -Ca ₃ (PO ₄) ₂	235.978	8.338	AC		Southard and Milner ^[143]
	177.247		AC	polymorph unknown	Soga <i>et al.</i> ^[153]
	235.978	8.338	optimized		this work
α -Ca ₂ P ₂ O ₇	197.485 ± 37.7	7.595	KEM		Butylin <i>et al.</i> ^[140]
	194.065	4.175	optimized		this work
β -Ca ₂ P ₂ O ₇	189.330 ± 0.1	-0.560	AC		Egan and Wakefield ^[158]
	189.328	-0.562	optimized		this work
γ -Ca ₂ P ₂ O ₇	149.040		AC	polymorph unknown	Soga <i>et al.</i> ^[153]
	189.025	-0.865	optimized		this work
Ca ₄ P ₆ O ₁₉	480.000	-14.171	optimized		this work
α -Ca(PO ₃) ₂	148.549	-3.591	optimized		this work
β -Ca(PO ₃) ₂	146.942 ± 0.1	-5.200	AC		Egan and Wakefield ^[165]
	146.440 ± 6.3	-5.700	KEM		Rat'kovskii <i>et al.</i> ^[164]
	152.298 ± 13.4	0.158	KEM		Butylin <i>et al.</i> , ^[140] Rat'kovskii <i>et al.</i> ^[163]
	136.817 ± 18.8	-15.324	DTA		Yaglov and Volkov ^[166]
γ -Ca(PO ₃) ₂	146.944	-5.196	optimized		this work
	119.371		AC	polymorph unknown	Soga <i>et al.</i> ^[153]
	144.356	-7.784	optimized		this work
Ca ₂ P ₆ O ₁₇	385.000	-33.671	optimized		this work
α -CaP ₄ O ₁₁	243.078	-23.453	optimized		this work
β -CaP ₄ O ₁₁	239.000	-27.531	optimized		this work

AC: adiabatic calorimetry; other abbreviations see Table II.

3. Ca₃(PO₄)₂ (C₃P)

Butylin *et al.*^[140] used the Knudsen effusion method to determine the ΔH_f° _{298.15 K} and S° _{298.15 K} of α' -Ca₃(PO₄)₂ and found -449.502 kJ mol⁻¹ (from the oxides) and 233.886 J mol⁻¹ K⁻¹, respectively. By investigating the system CaO-P₂O₅ at various water pressures, Riboud^[141] used the Clausius-Clapeyron relation to estimate the enthalpy of transition from α - to α' -Ca₃(PO₄)₂ at 1748 K (1475 °C). He found 73.220 kJ mol⁻¹, which is rather high for this kind of transformation; we consider his data as doubtful.

Smirnova *et al.*^[142] employed hydrochloric acid solution calorimetry to measure the standard enthalpy of formation of α -Ca₃(PO₄)₂ at 298.15 K (25.15 °C) and obtained -681.714 kJ mol⁻¹ from the oxides. Martin *et al.*^[122] found a slightly higher value, -686.262 kJ mol⁻¹ at 310.55 (37.4 °C), using isothermal calorimetry. The heat capacity of α -Ca₃(PO₄)₂ (Figure 3) was determined by low temperature adiabatic calorimetry between 15 K and 287 K (-258 °C and 14 °C) by Southard and Milner^[143] and the entropy S° _{298.15 K} was found to be 240.91472 J mol⁻¹ K⁻¹. Britzke and Veselovskii^[144] measured the heat content

of β - and α -Ca₃(PO₄)₂ between 871 K and 1512 K (598 °C and 1239 °C) using solution calorimetry and heat capacity data at high temperature were derived. Despite the fact that Britzke and Veselovskii^[144] corrected their raw data to make them in line with those of Southard and Milner,^[51] their heat capacity data are very scattered as can be seen in Figure 3. Britzke and Veselovskii's heat capacity data were fitted by Kelley^[145] using a polynomial equation which we adopted as it is. Britzke and Veselovskii^[144] also estimated (with some reserves) the enthalpy of transition between β - and α -Ca₃(PO₄)₂ at 1373 K (1100 °C) to be 18.828 kJ mol⁻¹.

For β -Ca₃(PO₄)₂, Berthelot^[146-148] measured the heat of neutralization of phosphoric acid by calcium hydroxide and obtained from the oxides a standard enthalpy of formation at 298.15 K (25.15 °C) of -687.572 kJ mol⁻¹ (values recalculated by Smirnova *et al.*^[142]). Matignon and Séon^[149] measured the heat of solution of Ca₃(PO₄)₂, CaO, and H₃PO₄ in 2N HCl and the heat of mixing of CaO and H₃PO₄; the data were then used by Richardson *et al.*^[150] to derive a standard enthalpy of formation at 298.15 K (25.15 °C) for β -Ca₃(PO₄)₂ of -686.176 kJ mol⁻¹. Jeffes (unpublished result cited in Pearson *et al.*^[124]) obtained a

Table XII. Heat Capacities of Compounds in the CaO-P₂O₅ System Optimized in the Present Study

Compound	Optimized (J mol ⁻¹ K ⁻¹)	Reference
α -Ca ₄ (PO ₄) ₂ O	317.5164047 + 0.089909858T - 6.287,652.317T ⁻²	Sokolov <i>et al.</i> ^[123]
β -Ca ₄ (PO ₄) ₂ O	317.5164047 + 0.089909858T - 6.287,652.317T ⁻²	C _P = C _P (α -Ca ₄ (PO ₄) ₂ O)
Ca ₁₀ (PO ₄) ₆ O ₂	720.1887247 + 0.421952098 T - 10.471,652.317T ⁻² 1294	C _P = C _P (α -Ca ₄ (PO ₄) ₂ O) + 2C _P (β -Ca ₃ (PO ₄) ₂)
α' -Ca ₃ (PO ₄) ₂	340.272	Britzke and Veselovskii ^[144] fitted by Kelley ^[145] and slightly modified
α -Ca ₃ (PO ₄) ₂	318.572	Britzke and Veselovskii ^[144] fitted by Kelley ^[145] and slightly modified
β -Ca ₃ (PO ₄) ₂	201.83616 + 0.16602112T - 2092000T ⁻² 330.536	Britzke and Veselovskii ^[144] fitted by Kelley ^[145] and slightly modified
α -Ca ₂ P ₂ O ₇	221.87752 + 0.06175584T - 4669344T ⁻²	Britzke and Veselovskii ^[144] fitted by Kelley ^[145]
298.15 K to 1413 K	318.6116	C _P = C _P (β -Ca ₂ P ₂ O ₇)
1413 K to 1627 K		
β -Ca ₂ P ₂ O ₇	221.87752 + 0.06175584T - 4669344T ⁻²	Egan and Wakefield ^[158] fitted by Kelley ^[145]
298.15 K to 1413 K	306.7918	
γ -Ca ₂ P ₂ O ₇	221.87752 + 0.06175584T - 4669344T ⁻²	C _P = C _P (β -Ca ₂ P ₂ O ₇)
298.15 K to 898 K	271.537416	
C ₄ P ₆ O ₁₉	606.434930568 + 0.138072T - 14778617.98248T ⁻² - 133.903999616T ^{-0.5} + 1,029,787,864 T ⁻³	C _P = 3C _P (β -Ca(PO ₃) ₂) + C _P (CaO)
298.15 K to 1500 K	182.54792 + 0.046024T - 4543824T ⁻²	C _P = C _P (β -Ca(PO ₃) ₂)
α -Ca(PO ₃) ₂	182.54792 + 0.046024T - 4543824T ⁻²	Egan and Wakefield ^[165] fitted by Kelley ^[145]
β -Ca(PO ₃) ₂	182.54792 + 0.046024T - 4543824T ⁻²	C _P = C _P (β -Ca(PO ₃) ₂)
γ -Ca(PO ₃) ₂	182.54792 + 0.046024T - 4543824T ⁻²	C _P = 2C _P (β -Ca(PO ₃) ₂) + C _P (H -P ₂ O ₅)
Ca ₂ P ₆ O ₁₇	343.4524331 + 0.428276402T - 12,604,021.135T ⁻² - 0.000112629T ² + 22,900.40185T ⁻¹	C _P = C _P (β -Ca ₂ P ₂ O ₇) + C _P (H -P ₂ O ₅)
298.15 K to 1200 K	160.9045131 + 0.382252402T - 8,060,197.135T ⁻² - 0.000112629T ² + 22,900.40185T ⁻¹	C _P = C _P (β -Ca ₂ P ₂ O ₇) + C _P (H -P ₂ O ₅)
α -CaP ₄ O ₁₁	160.9045131 + 0.382252402T - 8,060,197.135T ⁻² - 0.000112629T ² + 22,900.40185T ⁻¹	C _P = C _P (β -Ca ₂ P ₂ O ₇) + C _P (H -P ₂ O ₅)
298.15 K to 1200 K		

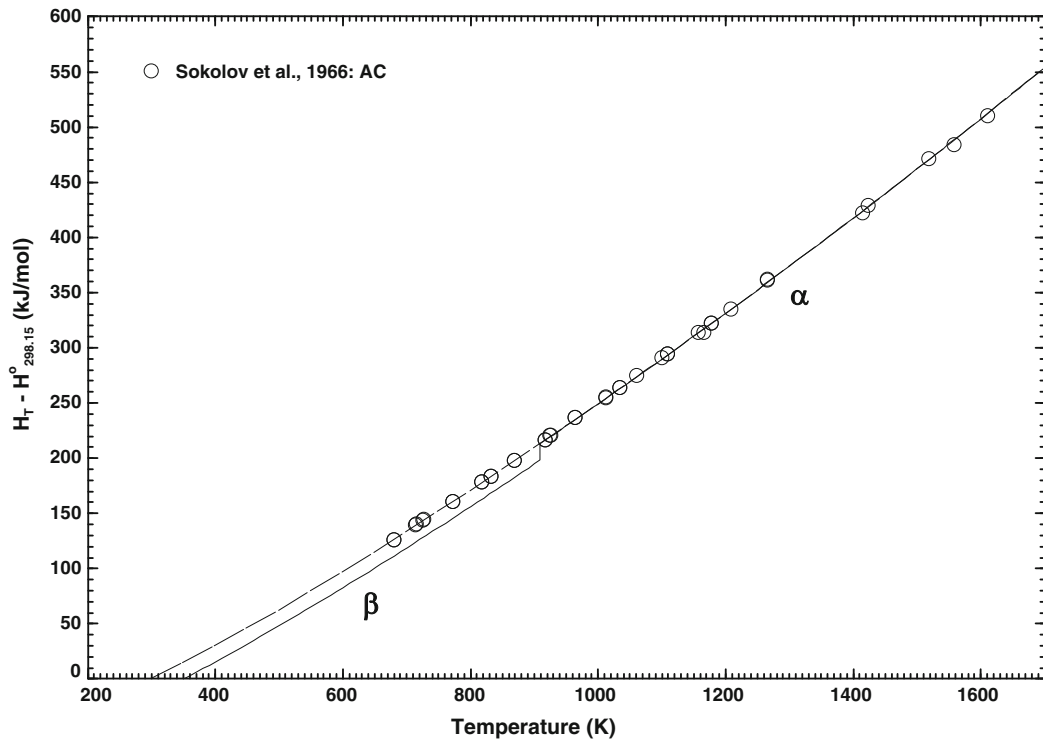


Fig. 2—Optimized heat content $H_T - H_{298.15K}^0$ of α - $\text{Ca}_4(\text{PO}_4)_2\text{O}$ along with experimental data of Sokolov *et al.*^[123].

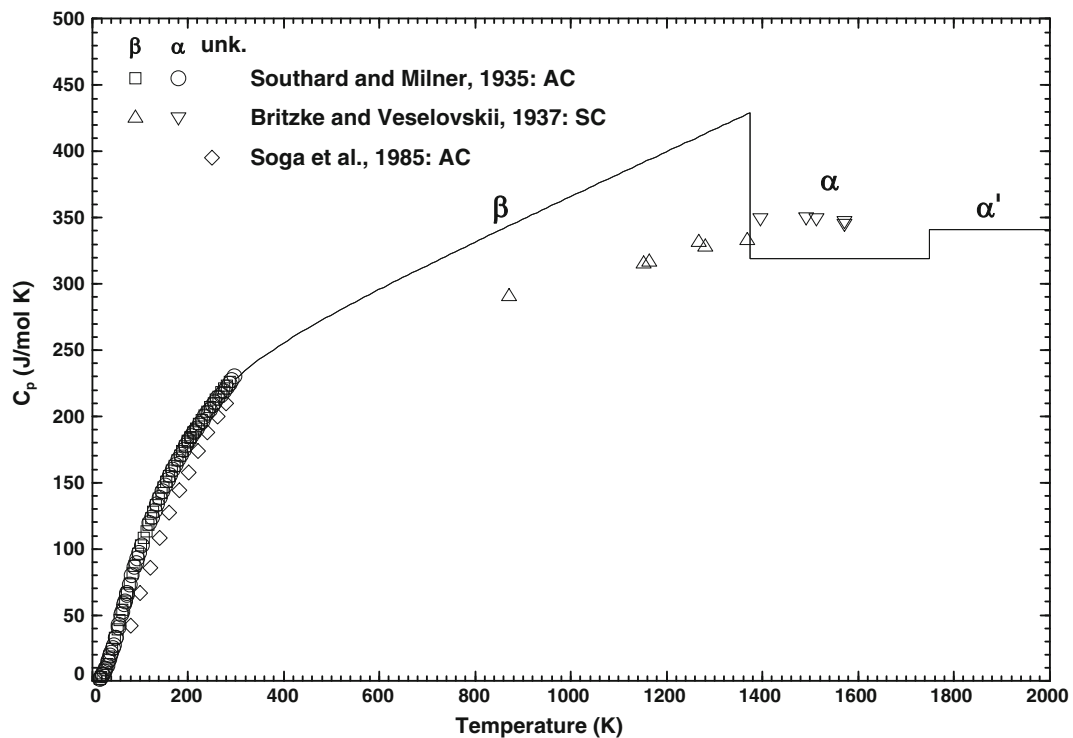


Fig. 3—Optimized heat capacity of α - and β - $\text{Ca}_3(\text{PO}_4)_2$ along with experimental data of Southard and Milner,^[143] Britzke and Veselovskii,^[144] and Soga *et al.*^[153] The polymorph employed by Soga *et al.*^[153] to make their measurements is unknown.

value of $-680.653 \text{ kJ mol}^{-1}$ at 348 K (75 °C) by hydrochloric acid solution calorimetry. Using the same technique, Smirnova *et al.*^[142] found $-702.634 \text{ kJ mol}^{-1}$ while

Meadcroft and Richardson^[151] obtained $-706.259 \pm 8.4 \text{ kJ mol}^{-1}$ at 308 K (35 °C). Jacques *et al.* (personal communication cited in Meadowcroft and Richardson^[151])

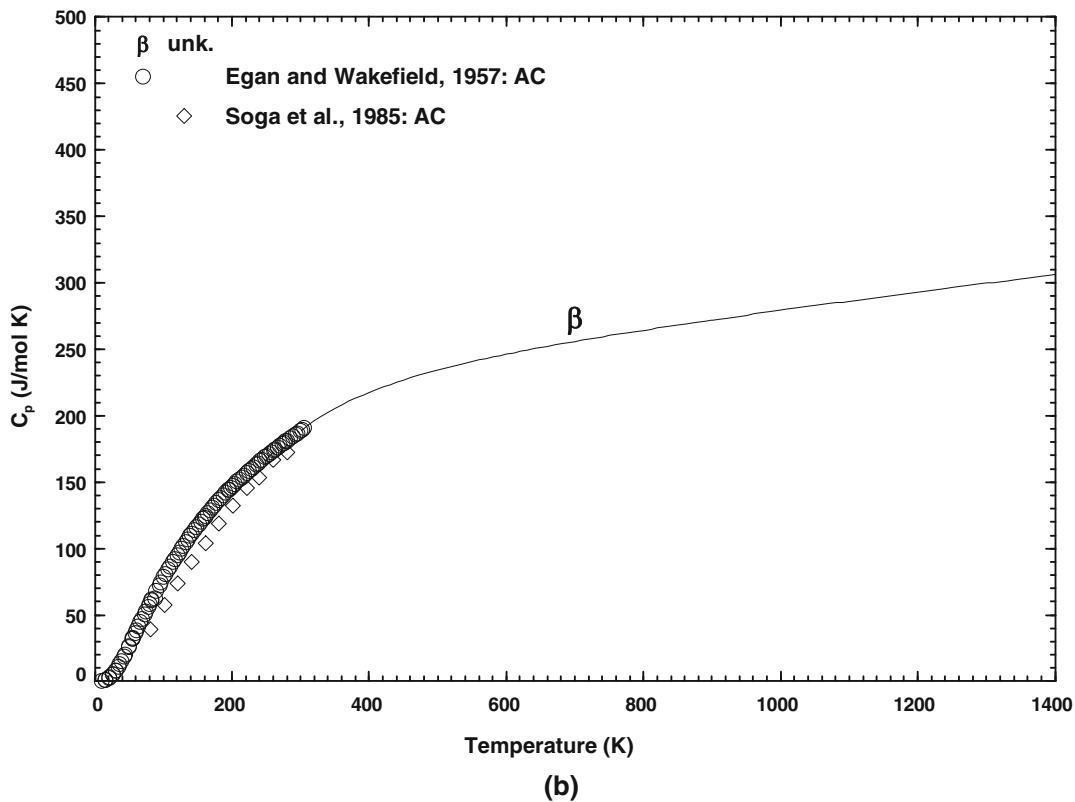
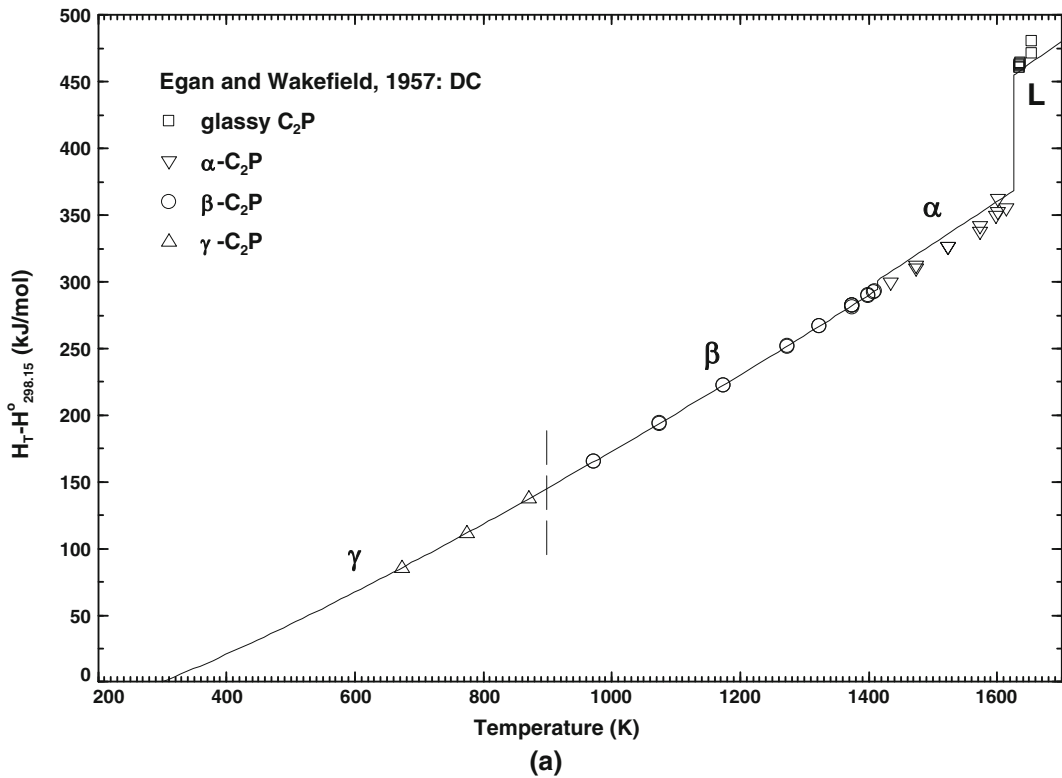


Fig. 4—Optimized (a) heat content $H_T - H_{298.15}^0$ of α -, β -, and γ - $Ca_2P_2O_7$ and its glass and (b) heat capacity C_p of β - $Ca_2P_2O_7$ along with experimental data of Egan and Wakefield^[158] and Soga *et al.*^[153] The polymorph employed by Soga *et al.*^[153] to make their measurements is unknown.

used solution calorimetry as well and reported a $\Delta H_f^{\circ}_{298.15\text{ K}}$ of $-717.954 \pm 16.7\text{ kJ mol}^{-1}$. More recently, Abdelkader *et al.*^[152] reported a much lower value, $-645.762\text{ kJ mol}^{-1}$, by measuring the heat of solution of

β - $Ca_3(PO_4)_2$ in a 9 wt pct nitric solution with an isoperibol calorimeter. The standard entropy at 298.15 K (25.15 °C), $S^{\circ}_{298.15\text{ K}}$, was determined by Southard and Milner^[143] with low temperature adiabatic calorimetry between 15 K and

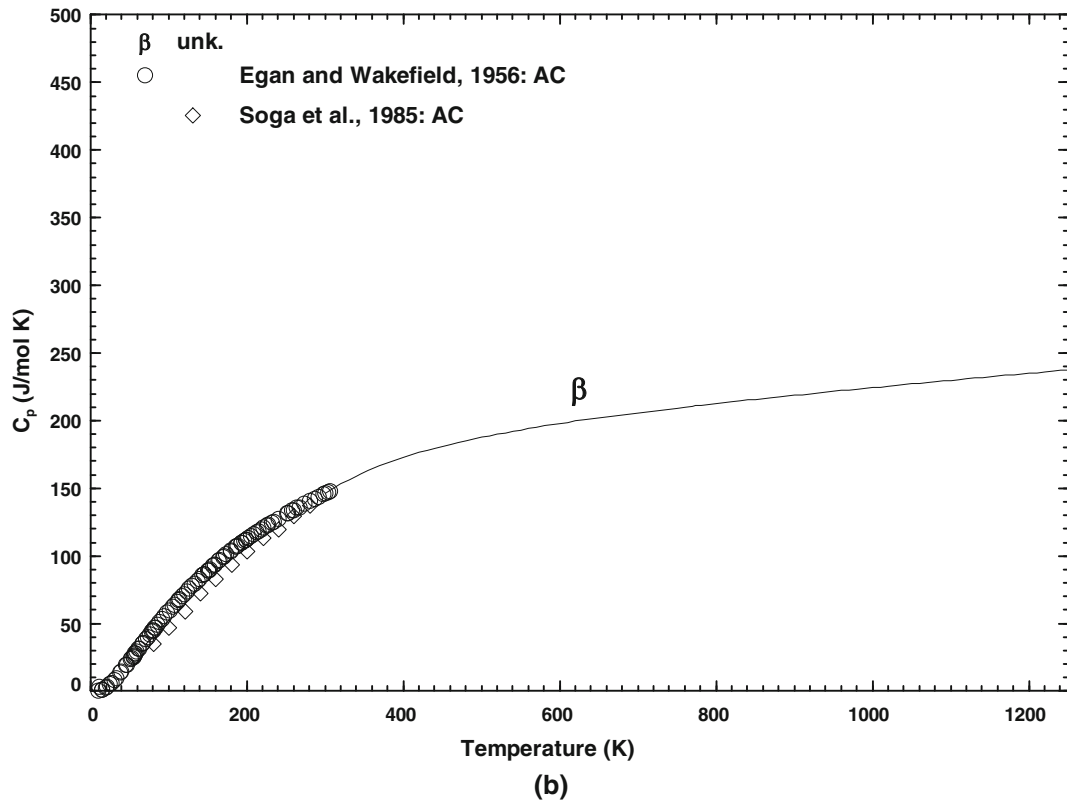
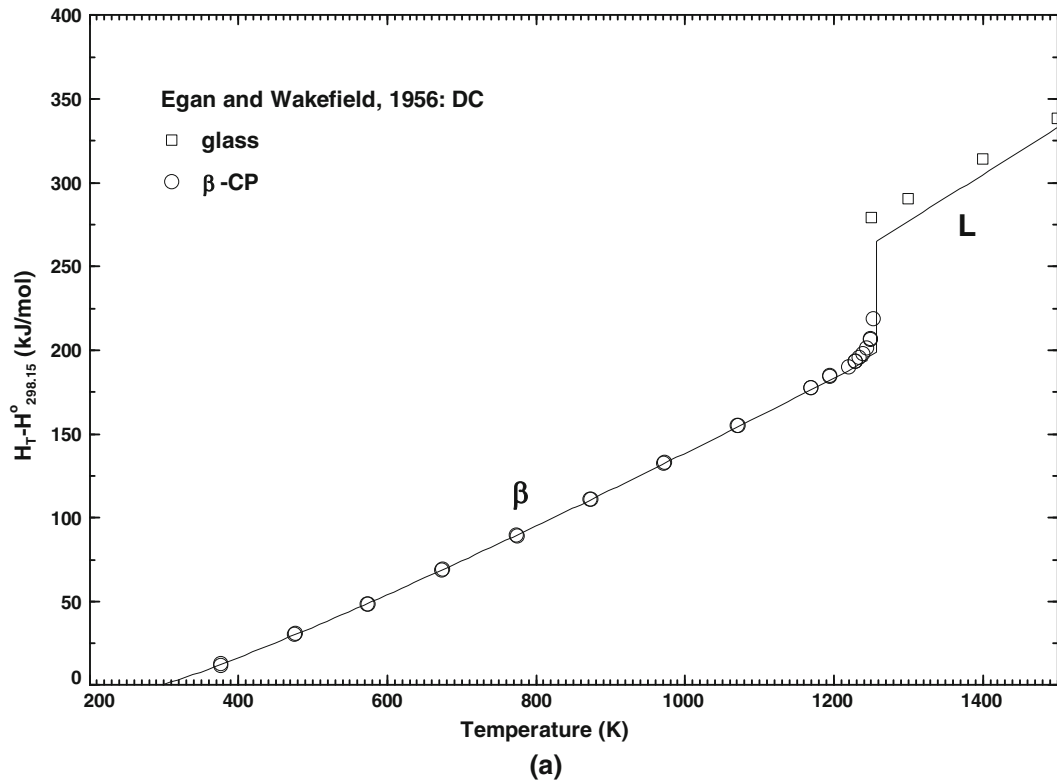


Fig. 5—Optimized (a) heat content $H_T - H_{298.15K}^0$ of β -Ca(PO₃)₂ and its glass and (b) heat capacity C_p of β -Ca(PO₃)₂ along with experimental data of Egan and Wakefield^[165] and Soga *et al.*^[153] The polymorph employed by Soga *et al.*^[153] to make their measurements is unknown.

300 K (−258 °C and 27 °C); they reported a value of 235.9776 J mol^{−1} K^{−1} by integrating their heat capacity data. Soga *et al.*^[153] prepared Ca₃(PO₄)₂ by crystallizing a

glass of the same composition; unfortunately, they did not indicate which polymorph (α' -, α -, or β -Ca₃(PO₄)₂) was obtained. Using low temperature adiabatic calorimetry,

they then determined the heat capacity between 80.1 K and 279.2 K (−192.9 °C and 6.2 °C) but did not calculate $S^{\circ}_{298.15\text{ K}}$. As can be seen in Figure 3, their C_P data are lower than those of Southard and Milner.^[143] By integrating the data of Soga *et al.*,^[153] one can obtain 177.247 J mol^{−1} K^{−1}, which is about 59 J mol^{−1} K^{−1} lower than the value measured by Southard and Milner^[143] for $\beta\text{-Ca}_3(\text{PO}_4)_2$.

The standard Gibbs energy of formation of $\text{Ca}_3(\text{PO}_4)_2$ was measured by Bookey^[126] between 1523 K and 1773 K (1250 °C and 1500 °C) using the reaction $4\alpha\text{-Ca}_3(\text{PO}_4)_2(\text{s}) + 5\text{H}_2(\text{g}) = 3\text{Ca}_4(\text{PO}_4)_2\text{O}(\text{s}) + \text{P}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$. As for $\text{Ca}_4(\text{PO}_4)_2\text{O}$, he determined the Gibbs energy of the reaction by passing a known volume of hydrogen over $\text{C}_3\text{P}(\text{s})$ and measuring the amount of $\text{H}_2\text{O}(\text{g})$ in the exit gas. Yama-zoye *et al.*^[154,155] determined the Gibbs energy of formation between 1423 K and 1523 K (1150 °C and 1250 °C) from the reaction $3\text{Ca}_4(\text{PO}_4)_2\text{O}(\text{s}) + \text{P}_2(\text{g}) + 5/2\text{O}_2(\text{g}) = 4\text{Ca}_3(\text{PO}_4)_2(\text{s})$. Molten copper contained in a graphite crucible was brought to equilibrium with $\text{C}_4\text{P}(\text{s})$ and $\text{C}_3\text{P}(\text{s})$ under a stream of pure CO gas at 1 atm. The Gibbs energy of formation of $\text{Ca}_3(\text{PO}_4)_2$ was also measured by Tagaya *et al.*^[131,132] between 1473 K and 1598 K (1200 °C and 1325 °C) using the reactions $3\text{Ca}_4(\text{PO}_4)_2\text{O}(\text{s}) + 2\text{P}_{\text{in Ag}} + 5\text{CO}(\text{g}) = 4\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 5\text{C}(\text{s})$ and $\text{Ca}_3(\text{PO}_4)_2(\text{s}) + \text{Ca}_{\text{in Ag}} + \text{CO}(\text{g}) = \text{Ca}_4(\text{PO}_4)_2\text{O}(\text{s})$. Mixtures of $\text{Ca}_3(\text{PO}_4)_2(\text{s})$ and $\text{Ca}_4(\text{PO}_4)_2\text{O}(\text{s})$ were equilibrated with silver-phosphorus alloys in graphite crucibles under CO and Ar mixtures. Recently, Nagai *et al.*^[133] determined the ΔG_f° between 1523 K and 1623 K (1250 °C and 1350 °C) using double Knudsen cell mass spectrometry. All the experimental data are converted to the standard Gibbs energy of formation of $\text{Ca}_3(\text{PO}_4)_2$ in Figures 6(a) and (b).

4. $\text{Ca}_2\text{P}_2\text{O}_7$ (C_2P)

Butylin *et al.*^[140] employed the Knudsen effusion method at 1555 K (1282 °C) and estimated the $\Delta H_f^{\circ}_{298.15\text{ K}}$ of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ to be −526.028 kJ mol^{−1} from the oxides; the standard entropy at 298.15 K (25.15 °C), $S^{\circ}_{298.15\text{ K}}$, was estimated to be 197.485 J mol^{−1} K^{−1}. Using the same technique between 1409 K and 1560 K (1136 °C and 1287 °C), Lopatin^[156] obtained a $\Delta H_f^{\circ}_{298.15\text{ K}}$ of −567.852 kJ mol^{−1}, but recently, Lopatin^[157] revised this result and reported a value of −548.852 kJ mol^{−1}. Egan and Wakefield^[158] measured the heat content of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ between 1473 K and 1626 K (1200 °C and 1353 °C) by drop calorimetry (Figure 4(a)) and the heat of fusion at 1626 K (1353 °C) was found to be −100.851 kJ mol^{−1}. Despite the fact that Egan and Wakefield^[158] did not observe directly the $\beta\text{-}\alpha$ transition, they reported a heat of transition of 6.786 kJ mol^{−1} at 1413 K (1140 °C). Similar enthalpy of transition was found by Mesmer and Irani^[159] using DTA and Jacob *et al.*^[160] using DSC; they obtained 6.360 kJ mol^{−1} at 1493 K (1220 °C) and 6.551 ± 0.7 kJ mol^{−1} at 1435 K (1162 °C), respectively.

For the $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ phase, no experimental measurements of the standard enthalpy of formation exist. The standard entropy at 298.15 K (25.15 °C), $S^{\circ}_{298.15\text{ K}}$, was determined to be 189.330 J mol^{−1} K^{−1} by Egan and

Wakefield^[158] using data obtained between 10 K and 305 K (−273 °C and 32 °C) with low temperature adiabatic calorimetry (Figure 4(b)). Egan and Wakefield^[158] also determined the heat content between 298 K and 1473 K (25 °C and 1200 °C) using drop calorimetry (Figure 4(a)), which allowed them to derive heat capacities at high temperatures. These heat capacity data were fitted by Kelley^[145] using a polynomial equation which is adopted in the present study. The enthalpy of transition from $\gamma\text{-}$ to $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ was measured by Mesmer and Irani^[159] using DTA and Jacob *et al.*^[160] using DSC; they obtained 1.674 kJ mol^{−1} at 1123 K (850 °C) and 1.074 ± 0.2 kJ mol^{−1} at 1074 K (801 °C), respectively.

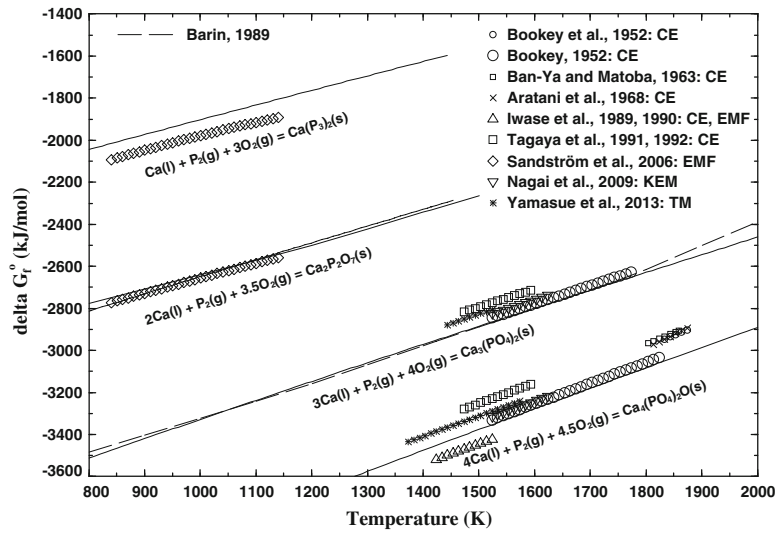
Little thermodynamic data exist for $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$. Mesmer and Irani^[159] determined the heat of solution of $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$ in 6N HCl at 308 K (35 °C) and derived a standard enthalpy of formation at 298.15 K (25.15 °C) of −571.116 ± 7.5 kJ mol^{−1} from the oxides. Egan and Wakefield^[158] measured the heat content of $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$ at 673 K, 773 K, and 873 K (400 °C, 500 °C, and 600 °C) and found that it is essentially the same as the $\beta\text{-}$ form. Soga *et al.*^[153] prepared $\text{Ca}_2\text{P}_2\text{O}_7$ by crystallizing a glass of the same composition; unfortunately, they did not indicate which polymorph ($\alpha\text{-}$, $\beta\text{-}$, or $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$) was obtained. Using low temperature adiabatic calorimetry, they then determined the heat capacity between 80.2 K and 280.4 K (−192.8 °C and 7.4 °C) but did not calculate $S^{\circ}_{298.15\text{ K}}$. As can be seen in Figure 4(b), their C_P data are lower than those of Egan and Wakefield.^[158] By integrating the data of Soga *et al.*,^[153] one can obtain 149.040 kJ mol^{−1}, which is about 40 J mol^{−1} K^{−1} lower than the value measured by Egan and Wakefield^[158] for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$.

Recently, the standard Gibbs energy of formation of $\text{Ca}_2\text{P}_2\text{O}_7$, ΔG_f° , was measured by Hoshino *et al.*^[161] between 1423 K and 1523 K (1150 °C and 1250 °C) and by Sandström *et al.*^[162] between 898 K and 1004 K (625 °C and 731 °C); both studies employed the solid-state emf method. Experimental data are compared in Figures 6(a) and (b).

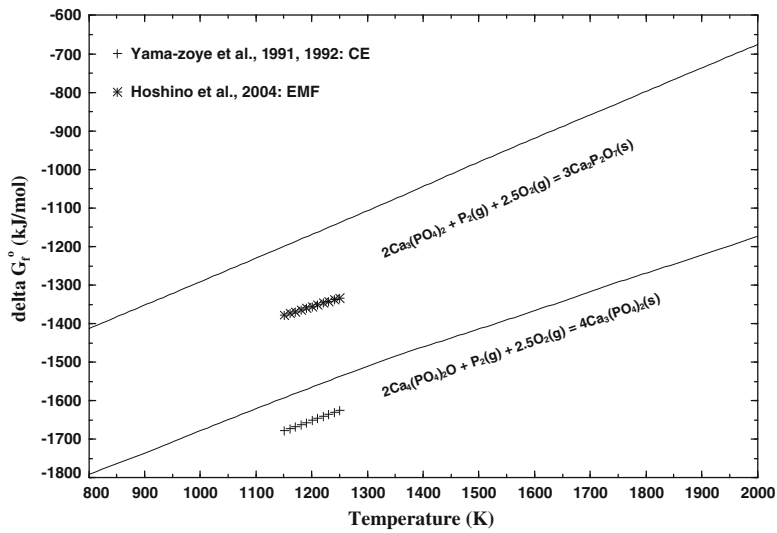
5. $\text{Ca}(\text{PO}_3)_2$ (CP)

No thermodynamic data exist for $\alpha\text{-Ca}(\text{PO}_3)_2$.

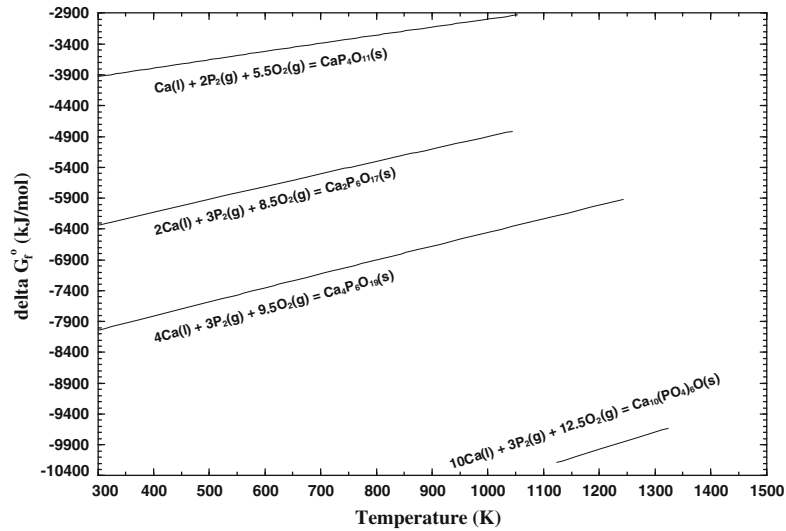
The standard enthalpy of formation at 298.15 K (25.15 °C) of $\beta\text{-Ca}(\text{PO}_3)_2$ was estimated from Knudsen effusion experiments at 1180 K and 1100 K (907 °C and 827 °C) by Rat'kovskii *et al.*^[163] and Butylin *et al.*,^[140] respectively; they both reported a value of −336.870 kJ mol^{−1} from the oxides. Using the same technique, Rat'kovskii *et al.*^[164] and Lopatin^[156] estimated the $\Delta H_f^{\circ}_{298.15\text{ K}}$ to be −315.950 and −342.942 kJ mol^{−1}, respectively. Later, Lopatin^[157] revised his data to −329.942 kJ mol^{−1}. The $S^{\circ}_{298.15\text{ K}}$ was determined by Egan and Wakefield^[165] using low temperature adiabatic calorimetry between 10 K and 306 K (−263 °C and 33 °C). The entropy measured by them is 146.940 J mol^{−1} K^{−1}, which is similar to the values obtained by Rat'kovskii *et al.*^[163,164] and Butylin *et al.*^[140] with the Knudsen effusion method: that is 146.440 and 152.298 J mol^{−1} K^{−1}, respectively. Yaglov and Volkov^[166] investigated the dehydration of



(a)



(b)



(c)

Fig. 6—Optimized standard Gibbs energies of formation of (a) $\text{Ca}_4(\text{PO}_4)_2\text{O}$ (C_4P), $\text{Ca}_3(\text{PO}_4)_2$ (C_3P), $\text{Ca}_2\text{P}_2\text{O}_7$ (C_2P) and $\text{Ca}(\text{PO}_3)_2$ (CP) from the elements along with experimental data of Bookey *et al.*,^[125] Bookey,^[126] Ban-Ya and Matoba,^[127] Aratani *et al.*,^[128] Iwase *et al.*,^[129,130] Tagaya *et al.*,^[131,132] Sandström *et al.*,^[162] Nagai *et al.*,^[133] and Yamasue *et al.*,^[134] (b) $\text{Ca}_3(\text{PO}_4)_2$ (C_3P) from $\text{Ca}_4(\text{PO}_4)_2\text{O}$ (C_4P) and $\text{Ca}_2\text{P}_2\text{O}_7$ (C_2P) from $\text{Ca}_3(\text{PO}_4)_2$ (C_3P), with experimental data of Yama-zoye *et al.*,^[154,155] and Hoshino *et al.*,^[161] and (c) $\text{Ca}_{10}(\text{PO}_4)_6\text{O}_2$ (C_{10}P_3), $\text{Ca}_4\text{P}_6\text{O}_{19}$, $\text{Ca}_2\text{P}_6\text{O}_{17}$, and $\text{CaP}_4\text{O}_{11}$ from the elements.

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ by DTA and found the $S^\circ_{298.15\text{ K}}$ for $\beta\text{-Ca}(\text{PO}_3)_2$ to be $136.817 \pm 18.8 \text{ J mol}^{-1} \text{ K}^{-1}$. Egan and Wakefield^[165] measured the heat content of $\beta\text{-Ca}(\text{PO}_3)_2$ between 375.80 K and 1253 K (102.65 °C and 979.85 °C) using drop calorimetry (Figure 5(a)) and derived its heat capacity data. These data were fitted by Kelley^[145] using a polynomial equation which is used in this study. The enthalpy of transition between γ - and $\beta\text{-Ca}(\text{PO}_3)_2$ at 963 K to 993 K (690 °C to 720 °C) was determined by Jackson *et al.*^[109] using DSC; they found $24 \pm 1 \text{ kJ mol}^{-1}$, a rather unreasonable value for this kind of transformation.

The standard enthalpy of formation at 298.15 K (25.15 °C) of $\gamma\text{-Ca}(\text{PO}_3)_2$ was determined by Volkov *et al.*^[167] who studied the dehydration of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot$

H_2O by DTA; they obtained $-340.636 \text{ kJ mol}^{-1}$ from the oxides. Soga *et al.*^[153] prepared $\text{Ca}(\text{PO}_3)_2$ by crystallizing a glass of the same composition; unfortunately, they did not indicate which polymorph (α -, β -, or γ - $\text{Ca}(\text{PO}_3)_2$) was obtained. Using low temperature adiabatic calorimetry, they then determined the heat capacity between 80.3 K and 280.7 K (-192.7 °C and 7.7 °C) but did not calculate $S^\circ_{298.15\text{ K}}$. As can be seen in Figure 5(b), their C_P data are lower than those of Egan and Wakefield.^[165] By integrating the data of Soga *et al.*,^[153] one can obtain $119.371 \text{ kJ mol}^{-1}$, which is about $28 \text{ J mol}^{-1} \text{ K}^{-1}$ lower than the value measured by Egan and Wakefield^[165] for $\beta\text{-Ca}(\text{PO}_3)_2$.

The standard Gibbs energy of formation of $\text{Ca}(\text{PO}_3)_2$ between 840 K and 1140 K (567 °C and 867 °C) was measured by Sandström^[162] using a solid-state emf cell. Experimental data are depicted in Figure 6(a).

6. $\text{CaP}_4\text{O}_{11}$ (CP_2)

No thermodynamic data exist for $\alpha\text{-CaP}_4\text{O}_{11}$.

The standard enthalpy of formation of $\beta\text{-CaP}_4\text{O}_{11}$ at 298.15 K (25.15 °C) was estimated by Golubchenko^[168] (cited and recalculated by Lopatin^[157]) using the Knudsen effusion method at 808 K to 923 K (535 °C to

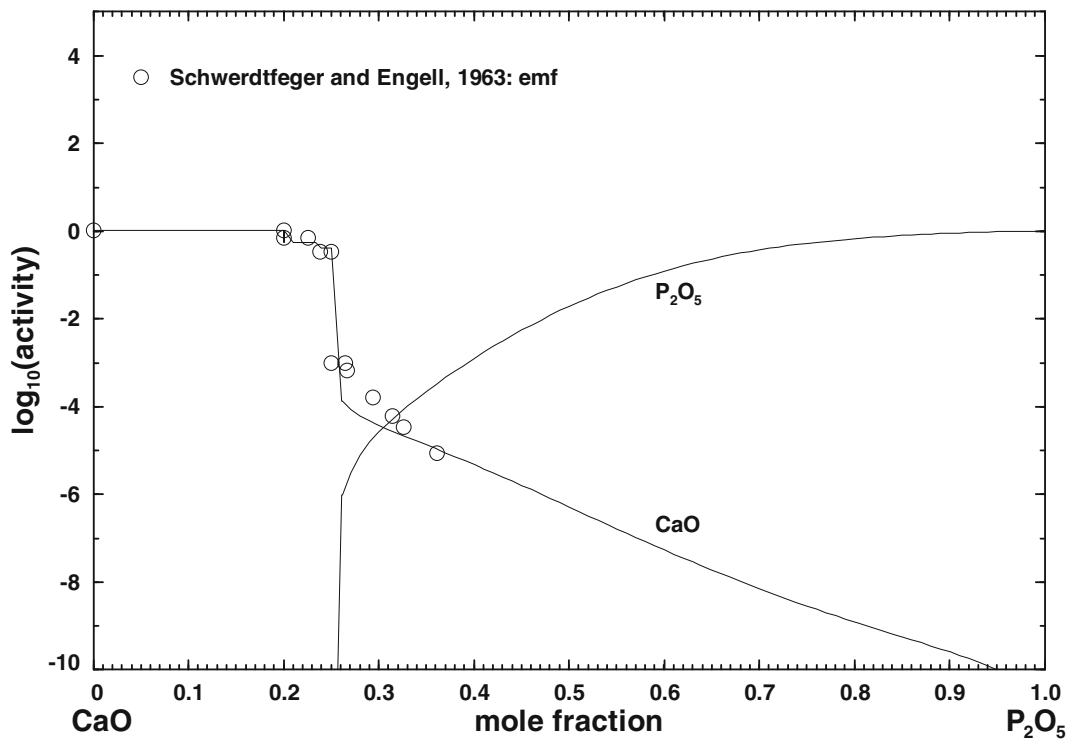


Fig. 7—Calculated activity of $\text{CaO}(\text{s})$ and $\text{P}_2\text{O}_5(\text{l})$ in $\text{CaO}\text{-P}_2\text{O}_5$ system at 1923 K (1650 °C) with experimental data of Schwerdtfeger and Engell.^[169]

Table XIII. Optimized Quasichemical Model Parameters of the $\text{CaO}\text{-P}_2\text{O}_5$ Liquid Phase

Coordination numbers: $Z_{\text{CaCa}}^{\text{Ca}} = 1.37744375$ $Z_{\text{P}_2\text{O}_3\text{P}_2\text{O}_3}^{\text{P}_2\text{O}_3} = 4.13220000$

$$A_{\text{Ca-P}_2\text{O}_3}^0 = -435,868.2 + 41.29608T - 37,656X_{\text{CaCa}}^1 - 126,147.6X_{\text{P}_2\text{O}_3\text{P}_2\text{O}_3}^1 - (186,955.2 - 46.0198T)X_{\text{P}_2\text{O}_3\text{P}_2\text{O}_3}^2 + 74,335.1$$

$X_{\text{P}_2\text{O}_3\text{P}_2\text{O}_3}^i$ (J/mol and $\text{J mol}^{-1} \text{ K}^{-1}$)

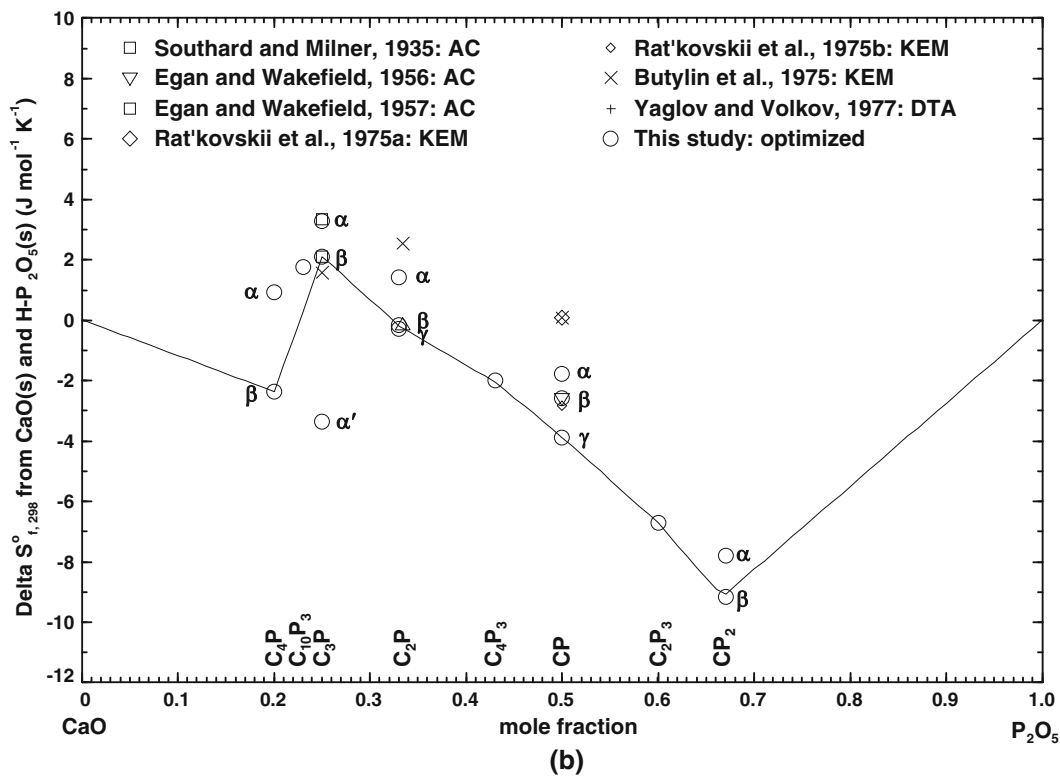
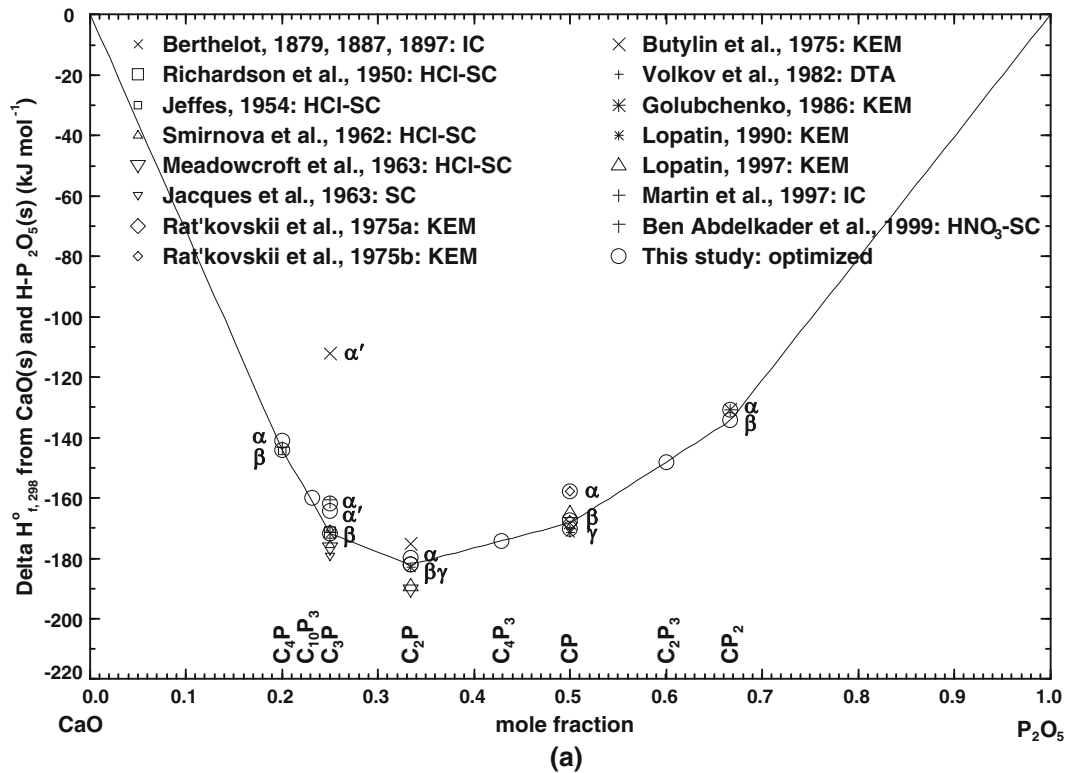


Fig. 8—Calculated and experimentally determined (a) enthalpies of formation at 298.15 K (25.15 °C) with experimental data of Berthelot,^[146–148] Richardson *et al.*,^[150] Jeffes cited in Pearson *et al.*,^[124] Smirnova *et al.*,^[142] Meadowcroft *et al.*,^[151] Jacques *et al.* cited in Meadowcroft and Richardson,^[151] Rat'kovskii *et al.*,^[163] Rat'kovskii *et al.*,^[164] Butylin *et al.*,^[140] Volkov *et al.*,^[167] Golubchenko,^[168] Lopatin,^[156] Lopatin,^[157] Martin *et al.*,^[122] and Ben Abdelkader *et al.*,^[152] and (b) entropies of formation at 298.15 K (25.15 °C) of the compounds with experimental data of Southard and Milner,^[143] Egan and Wakefield,^[165] Egan and Wakefield,^[158] Rat'kovskii *et al.*,^[163] Rat'kovskii *et al.*,^[164] Butylin *et al.*,^[140] and Yaglov and Volkov.^[166] The solid lines are calculated values connecting the polymorphs stable at 298.15 K (25.15 °C). Note that the reference state of P₂O₅ is hexagonal P₂O₅ (strictly speaking, hexagonal P₂O₅ is metastable at 298.15 K (25.15 °C) but is the most commonly used polymorph as a reference state for solid P₂O₅). Note also that the enthalpies and entropies of formation are here given for one mole of components CaO plus P₂O₅.

650 °C); he obtained a value of $-392.97 \text{ kJ mol}^{-1}$ from the oxides.

7. Liquid

Using a galvanic cell, Schwerdtfeger and Engell^[169] measured the activity of CaO(s) in the CaO-rich part of liquid CaO-P₂O₅ at 1923 K (1650 °C). Experimental data (Figure 7) show a sharp decrease in the CaO activity at 0.25 mol fraction of P₂O₅.

III. THERMODYNAMIC MODEL

A. Stoichiometric Compounds

The Gibbs energy of stoichiometric compounds can be described by:

$$G_T^\circ = H_T^\circ - TS_T^\circ, \quad [1]$$

$$H_T^\circ = \Delta H_{298.15\text{K}}^\circ + \int_{T=298.15\text{K}}^T C_p dT, \quad [2]$$

$$S_T^\circ = S_{298.15\text{K}}^\circ + \int_{T=298.15\text{K}}^T \left(\frac{C_p}{T} \right) dT, \quad [3]$$

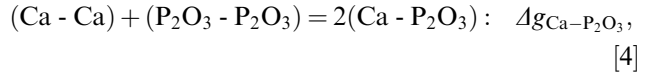
where $\Delta H_{298.15\text{K}}^\circ$ is the enthalpy of formation of a given species from pure elements ($\Delta H_{298.15\text{K}}^\circ$ of elemental species stable at 298.15 K (25.15 °C) and 1 atm are assumed as 0 J/mol; reference state), $S_{298.15\text{K}}^\circ$ is the entropy at 298.15 K (25.15 °C), and C_p is the heat capacity.

B. Liquid Phase

The modified quasichemical model (MQM),^[170] which takes into account the short-range-ordering (SRO) of second-nearest-neighbor (SNN) cations in liquid silicate, is used to describe the thermodynamics of the liquid oxide melt. Since oxygen is always connected to cations in oxide melt systems, the breakage of the P₂O₅ network by CaO can be simulated by consideration of SRO of SNN cations. In the CaO-P₂O₅ liquid solution, both PO₄³⁻ and P₂O₇⁴⁻ are the basic building units of P₂O₅. Strictly speaking, both P₂O₇⁴⁻ and PO₄³⁻ can exist in the liquid phase, but for the sake of simplicity in the present thermodynamic modeling, we use only P₂O₇⁴⁻. We already used this for the SiO₂-P₂O₅ system and successfully explained the phase diagram and in particular the liquidus of SiO₂.^[20]

In order to adopt P₂O₇⁴⁻ as a building unit of P₂O₅ in the MQM, P₂O₃⁴⁺, which can be surrounded by four broken oxygen to form P₂O₇⁴⁻ (this is similar to Si⁴⁺ surrounded by four broken oxygen to form SiO₄⁴⁻), was used as a cation species for the P₂O₅ component. To reproduce the short range ordering (minimum enthalpy of mixing of liquid) occurring at the Ca₃P₂O₈ composition, the coordination numbers of the cations were set in the model to be 1.37745 for Ca²⁺ and 4.1322 for

P₂O₃⁴⁺. The quasichemical reaction between cations in liquid CaO-P₂O₅ can be expressed as:



where $\Delta g_{\text{Ca}-\text{P}_2\text{O}_3}$ is the Gibbs energy of the quasichemical Reaction [4].

The molar Gibbs energy of the liquid CaO-P₂O₅ solution in the MQM can then be expressed as:

$$G_{\text{Liquid}} = n_{\text{CaO}} G_{\text{CaO}}^\circ + n_{\text{P}_2\text{O}_5} G_{\text{P}_2\text{O}_5}^\circ - T \Delta S^{\text{conf}} + (n_{\text{Ca}-\text{P}_2\text{O}_3} \Delta g_{\text{Ca}-\text{P}_2\text{O}_3} / 2), \quad [5]$$

where, G_{CaO}° and $G_{\text{P}_2\text{O}_5}^\circ$ are the molar Gibbs energies of pure liquid CaO and P₂O₅, ΔS^{conf} is the configurational entropy of mixing given by a random distribution of the (Ca-Ca) (P₂O₃-P₂O₃) and (Ca-P₂O₃) pairs in the one-dimensional Ising approximation, n_{CaO} and $n_{\text{P}_2\text{O}_5}$ are the numbers of moles of CaO and P₂O₅, and $n_{\text{Ca}-\text{P}_2\text{O}_3}$ is the number of moles of (Ca-P₂O₃) pairs in one mole of CaO-P₂O₅ solution. The term $\Delta g_{\text{Ca}-\text{P}_2\text{O}_3}$ is the model parameter to reproduce the Gibbs energy of the liquid phase of the binary CaO-P₂O₅ system, which is expanded as a polynomial in terms of the pair fractions, as follows:

$$\Delta g_{\text{Ca}-\text{P}_2\text{O}_3} = \Delta g_{\text{Ca}-\text{P}_2\text{O}_3}^0 + \sum g_{\text{Ca}-\text{P}_2\text{O}_3}^{i0} (X_{\text{Ca}-\text{Ca}})^i + \sum g_{\text{Ca}-\text{P}_2\text{O}_3}^{0j} (X_{\text{P}_2\text{O}_3-\text{P}_2\text{O}_3})^j, \quad [6]$$

where $\Delta g_{\text{Ca}-\text{P}_2\text{O}_3}^0$, $g_{\text{Ca}-\text{P}_2\text{O}_3}^{i0}$ and $g_{\text{Ca}-\text{P}_2\text{O}_3}^{0j}$ are adjustable model parameters which can be functions of temperature. The details of the model including the expression of ΔS^{conf} can be found elsewhere.^[170]

IV. THERMODYNAMIC OPTIMIZATION

Thermodynamic optimization (modeling) of the present system was carried out based on the critical evaluation of all the experimental data discussed in Section II using the thermodynamic model described in Section III. Since thermodynamic data for the liquid are scarce and those for the solid compounds are abundant, the thermodynamic properties of the solid phases were first determined followed by the preliminary optimization of the model parameters of the liquid phase to reproduce the phase diagram. In the final stage, the thermodynamic parameters of both solids and liquid were optimized to reproduce all reliable experimental data within experimental error limits as much as possible. In the case of the solid phases C₁₀P₃, C₄P₃, C₂P₃, and CP₂ for which little or no thermodynamic data are available, heat capacities were first evaluated by summing the C_p of known adjacent compounds as listed in Table XII. The $\Delta H_{298.15\text{K}}^\circ$ and $S_{298.15\text{K}}^\circ$ of the compounds were then evaluated to reproduce the phase diagram. The results of the optimization are compared with experimental data in Figures 1 through 7 and Tables II through VII and IX through XII. In general, all the experimental data are well reproduced within experimental error limits.

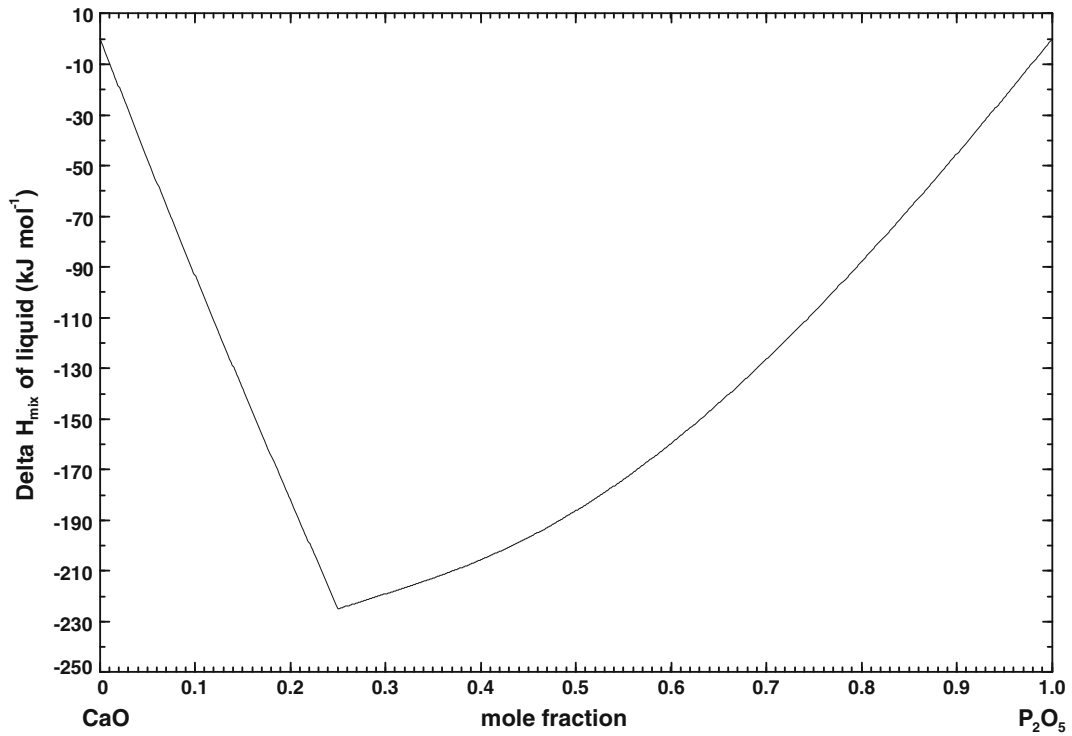


Fig. 9—Calculated enthalpy of mixing of the liquid phase at 1873 K (1600 °C).

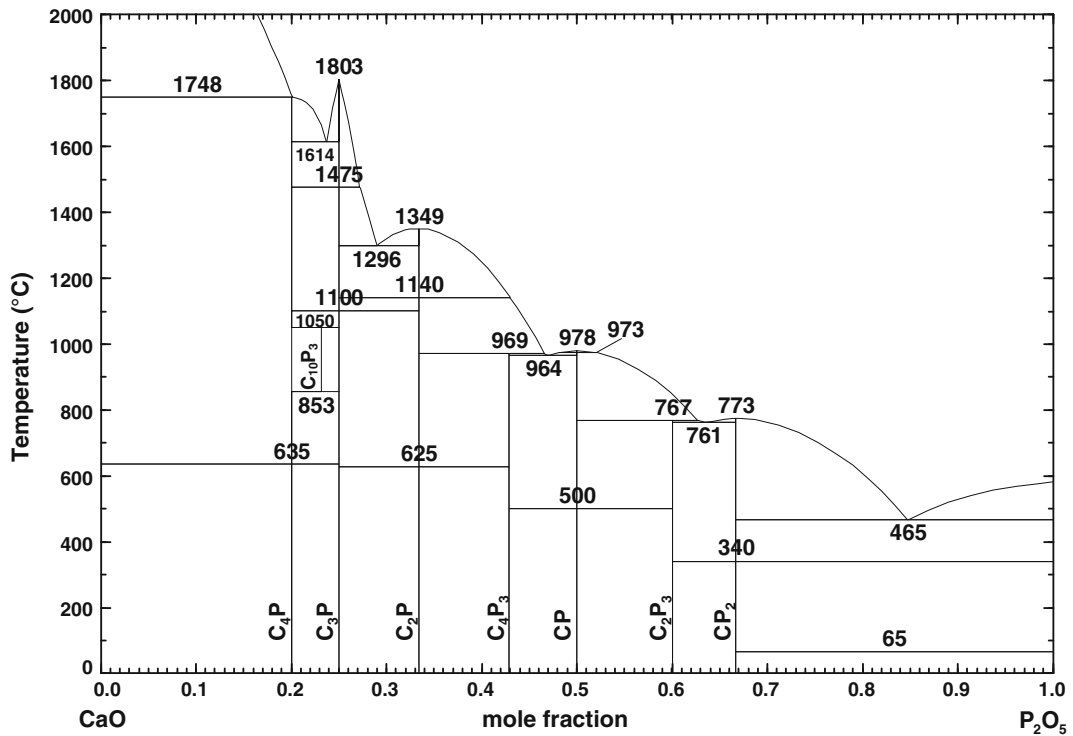


Fig. 10—The optimized binary CaO-P₂O₅ system. Temperatures are in degree Celsius.

The phase diagram data of the CaO-P₂O₅ system are in general well reproduced in the present optimization except for the liquidus of C₄P; the melting temperature of C₄P being reproduced slightly outside experimental

error limits. Optimized liquid model parameters are listed in Table XIII. In order to reproduce the sharp liquidus of C₃P, relatively large temperature dependent terms were needed for the $\Delta g_{\text{Ca-P}_2\text{O}_3}^0$ parameter.

During the optimization, we were also able to resolve the discrepancies observed in the Gibbs energy of formation of the compounds. Figure 6 shows the calculated Gibbs energy of formation of intermediate compounds in the CaO-P₂O₅ system along with experimental data. Some original experimental data^[125–134] were given as the Gibbs energy of formation from CaO, $\underline{Q}_{\text{in Fe}}$ or $\underline{P}_{\text{in Fe}}$; they were converted to the Gibbs energy of formation from elemental references using the Gibbs energy changes of the reactions $\text{Ca(l)} + \text{O}_2(\text{g}) = \text{CaO(s)}$ from FactSage (Bale *et al.*^[121]), $2.5\text{O}_2(\text{g}) = 5\underline{O}_{\text{in Fe}}$ from Sakao and Sano^[135] and Elliot and Gleiser,^[136] $\text{P}_2(\text{g}) = 2\underline{P}_{\text{in Fe}}$ from Yamamoto *et al.*,^[139] and $0.5\text{P}_2(\text{g}) = \underline{P}_{\text{in Ag}}$ from Ban-Ya and Suzuki^[138] and Yamamoto *et al.*^[139] The Gibbs energy of formation can be indirectly calculated from known $\Delta H_{298.15\text{K}}^\circ$, $S_{298.15\text{K}}^\circ$, and heat capacity. According to our optimization, the experimental Gibbs energy of formation of C₄P and C₃P measured by Bookey *et al.*^[126] and Nagai *et al.*^[133] are more consistent with other experimental thermodynamic property data in Tables IX through XII than those by Bookey *et al.*,^[125] Ban-Ya and Matoba,^[127] Iwase *et al.*,^[129,130] Tagaya *et al.*,^[131,132] and Yamasue *et al.*^[134] The experimental emf data of C₂P determined by Sandström *et al.*^[162] are also consistent with other data in Tables IX through XII. However, the Gibbs energy of formation of CP from the emf measurements of Sandström *et al.*^[162] is inconsistent with the enthalpy, entropy and heat capacity data of the same compound listed in Tables IX through XII. The optimized Gibbs energy of CP is about 50 kJ mol⁻¹ higher than the experimental data reported by Sandström *et al.*^[162]

As can be seen in Figure 8(a), the optimized enthalpies of formation of the compounds at 298.15 K (25.15 °C) (here given for 1 mol of components CaO plus P₂O₅) are in good agreement with experimental data except for the enthalpy measured by Butylin *et al.*^[140] for α' -Ca₃(PO₄)₂ (α' -C₃P), which is far off from the trend observed for other data. The optimized enthalpies of formation reach a minimum of about -180 kJ mol⁻¹ at the Ca₂P₂O₇ (C₂P) composition. This is almost four times more negative than that for the CaO-SiO₂ system.^[171] The optimized entropies of formation of the compounds at 298.15 K (25.15 °C) (Figure 8(b); also here given for one mole of components CaO plus P₂O₅) are also in good agreement with experimental data except for the entropy of β -Ca(PO₃)₂ (β -CP) determined by Yaglov and Volkov^[166] using DTA (a not reliable technique for entropy determination) and, again, by Butylin *et al.*^[140] for α' -C₃P. It is not clear why Butylin *et al.*^[140] failed to obtain reliable enthalpy and entropy of formation for α' -C₃P using the Knudsen effusion method.

The enthalpies of fusion of C₂P and CP are well reproduced as shown in Figures 4 and 5. The enthalpy of mixing of the liquid phase at 1773 K (1500 °C) is calculated from the present optimization in Figure 9; like the enthalpies of formation of the solid compounds, the liquid shows a minimum at 0.25 mol fraction of P₂O₅ and reaches -225 kJ mol⁻¹. Unfortunately, there is no experimental enthalpy data for the liquid. However, our calculated enthalpy must be reasonable as

judged from the well reproduced enthalpies of melting of Ca₂P₂O₇ and CaP₂O₆ in Figures 4 and 5. The sharp change in the enthalpy of mixing of the liquid phase at 0.25 mol fraction of P₂O₅ is also consistent with the activity of CaO in Figure 7 and the sharp liquidus of C₃P as shown in the phase diagram of Figure 1. For the sake of clarity, the optimized binary CaO-P₂O₅ system is depicted in Figure 10 without experimental data.

A final note must be made about the CaO melting point that was employed in this study. Using quasi-containerless laser heating in various controlled atmospheres, Manara *et al.*^[172] just recently located the CaO melting point at 3222 ± 25 K (2949 ± 25 °C), which is 377 K (377 °C) above the value (2845 K; 2572 °C) we used in our optimization of the CaO-P₂O₅ system. The new melting point obtained by Manara *et al.*^[172] is in agreement with earlier measurements performed by Foex^[173] [3223 K (2950 °C)], Traverse and Foex^[174] [3200 K (2927 °C)] and Yamada^[175] [3178 K (2905 °C)] and the value recommended in the JANAF Tables^[176] [3200 K (2927 °C)] whereas the melting point employed by us is in agreement with previous determinations made by Noguchi *et al.*^[177] [(2863 K) 2590 °C], Panek^[178] [2890 K (2617 °C)], Shevchenko^[179] [2833 K (2560 °C)], and Hlaváč^[180] [2886 K (2613 °C)]. According to Manara *et al.*,^[172] the difference observed between the two experimental datasets [one with temperatures around 3200 K (2927 °C) and one with temperatures around 2868 K (2595 °C)] is due to the oxidizing/reducing conditions in which the CaO melting point was measured in the various studies. In this regard, the Ca-O binary system provides some clues about the CaO melting point. In this system, the CaO liquidus, which is metastable, was experimentally determined by Bevan and Richardson^[181] using thermal analysis, by Fischbach^[182] using DTA and the quenching method, and by Zaitsev and Mogutnov^[183] using the quenching method. Data collected by Fischbach^[182] are slightly at odds with those of Bevan^[181] and Zaitsev and Mogutnov^[183] but according to Fischbach^[182] himself, this may be caused by segregation effects in his samples. Extrapolation of the metastable CaO liquidus data toward pure CaO points to a melting temperature of about 2800 K (2527 °C), which is in agreement with the value [2845 K (2572 °C)] we used in our optimization of the CaO-P₂O₅ system. The melting point employed by us is actually based on the optimization of the CaO-SiO₂ system by Pelton and Blander,^[184] the CaO-MgO, CaO-FeO, and CaO-MnO systems by Wu *et al.*,^[185] and the Ca-O system by Lindberg and Chartrand.^[186] In these phase diagram assessments, the CaO melting point was obtained by extrapolating CaO liquidus data, collected at low temperatures, toward pure CaO; this points to a melting temperature of 2845 K (2572 °C).

V. SUMMARY

The CaO-P₂O₅ system was successfully optimized by performing a comprehensive evaluation of all available experimental phase diagram and thermodynamic data. The CaO-P₂O₅ system is one of the most energetically

negative oxide systems among all well-known binary solid oxide systems. In the present study, the Gibbs energy of the liquid phase was well described by the MQM taking into account the short range ordering in the liquid state. The discrepancies in the Gibbs energy of formation of the compounds were also resolved as the results of the thermodynamic optimization. Phase diagram data are well reproduced except for the liquidus of $\text{Ca}_4(\text{PO}_4)_2\text{O}$ (C_4P) which is slightly away from the experimental error range. The model with optimized model parameters can be used to calculate any thermodynamic properties in the system. The obtained thermodynamic database is being expanded to the multicomponent system $\text{Na}_2\text{O-MgO-CaO-FeO-Fe}_2\text{O}_3\text{-MnO-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5$ for applications related to the glassmaking and steelmaking processes.

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