Thermodynamic Description of the Pb-O System

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The phase relations and thermodynamic properties of the Pb-O system are reviewed and assessed. The transformation temperature between PbO and Pb_3O_4 was also experimentally reinvestigated. A model description of the Pb-O system is then proposed and thermodynamic parameters are optimized. The values calculated from the resulting consistent set of Gibbs energy functions are compared with experimental data and discussed.

1. Introduction

The aim of this study is to provide a thermodynamic model description of the Pb-O system that will be used for the calculation of phase equilibria in multicomponent systems. The Pb-O system was recently reviewed by [88Wri], who gave an exhaustive summary of the numerous studies and discussed the controversies and uncertainties related to the subject. The system can be roughly described in two parts.

Between the compositions Pb and PbO, no solid compounds have been found except for the terminal compositions. On the metallic side, Pb is stable in the fcc structure, and on the oxide side, PbO has two stable modifications. The liquid phase exhibits a large miscibility gap that extends up to the highest temperature of the reported measurements.

Between the compositions PbO and PbO_2, numerous oxides of Pb have been observed. The number, crystal structure, composition, and relative stability of the possible phases in this part of the system add up to a complex problem with still quite a few uncertainties. Many contradictory results have been reported, and the reasons are manifold. Various phases have closely related crystal structures, which could easily lead to disagreement on the phase relations and compositions due to differences in the accuracy of the XRD analysis. Early work could not benefit from such analysis. As a result, many variations in the nomenclature exist. Moreover, the relative stability among some phases is small, the kinetics of many reactions

Table 1 Thermodynamic Properties of Lead Oxides at 298.15 K

Phase	$\Delta_f H^{298}$, J/mol	Reference	$\Delta_f G^{298}$, J/mol	Reference	S^{298}, J/mol · K	Reference
PbO-L	−219 409	[85Cha]	−189 041(a)	[23Smi]	65.3	[58Kin]
	−219 055	This work	−189 318(a)	[32Spe]	66.3	[85Cha]
			−189 283	[85Cha]	66.3	This work
			−188 937	This work		
PbO-M	−218 062	[70Esp]	−188 711(a)	[32Spe]	67.4	[58Kin]
	−218 062	[85Cha]	−188 647	[85Cha]	68.7	[60Kos]
	−217 442	This work	−188 036	This work	68.7	[85Cha]
					68.7	This work
Pb_3O_4-T	−718 686	[70Esp]	−597 308 (a)	[34And]	212	[85Cha]
	−718 686	[85Cha]	−617 190	[63Cha]	207	This work
	−733 871	This work	−601 606	[85Cha]		
			−615 297	This work		
$Pb_{12}O_{17}$	−3 032 827	This work	−2 508 630	This work	791	This work
$Pb_{12}O_{19}$	−3 111 415	This work	−2 533 940	[63Cha]	856	This work
			−2 554 043	This work		
PbO_2-I	−274 512	[70Esp]	−218 949 (a)	[29Mil]	76.4	[29Mil]
	−274 470	[85Cha]	−215 397	[85Cha]	71.8	[68Dui]
	−281 720	This work	−222 674	This work	71.8	[85Cha]
					71.8	This work

(a) Value recalculated from the cell reaction by [85Cha] using their own auxiliary data.

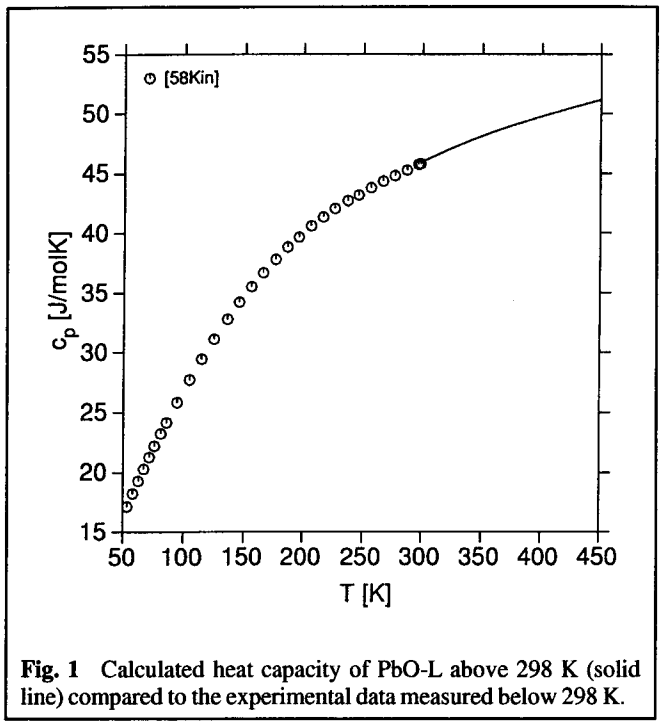

Fig. 1 Calculated heat capacity of PbO-L above 298 K (solid line) compared to the experimental data measured below 298 K.

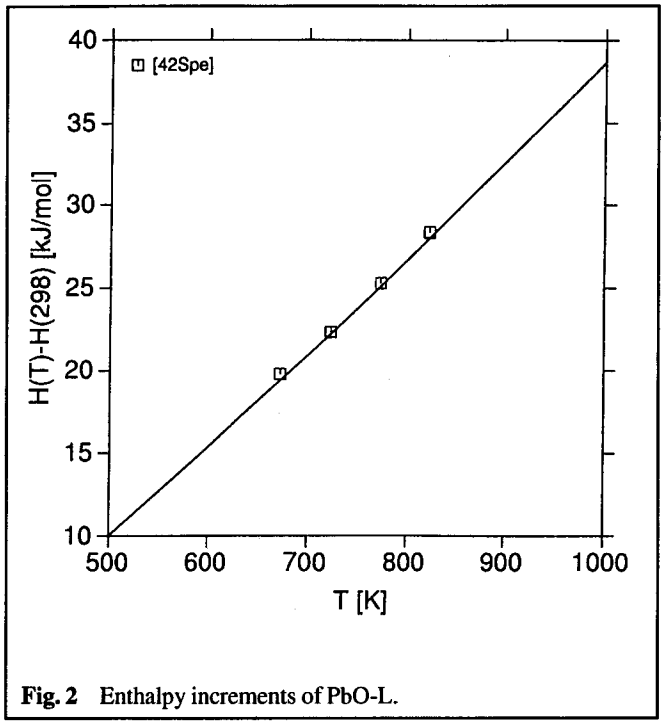

Fig. 2 Enthalpy increments of PbO-L.

are slow, and some failure to achieve the equilibrium state could arise easily. The vapor phase can also play a significant role. This article follows the nomenclature adopted by [88Wri], who also summarizes structure data and complementary information.

Various parts of the Pb-O system have been assessed by different authors, but a consistent thermodynamic description through the entire composition range is still lacking. This article reviews the thermodynamic data and presents a consistent set of Gibbs energy functions for the Pb-O system.

2. Experimental Data

The following summary of the experimental data on the Pb-O system focuses on the thermodynamic properties of the stable phases and should be seen as complementary to the review of [88Wri].

2.1 PbO

Lead monoxide has two stable modifications: tetragonal PbO-L (litharge, red PbO, αPbO) stable at lower temperatures and lower pressures, and orthorhombic PbO-M (massicot, yellow PbO, βPbO) stable at higher temperatures and pressures. Some authors [50Kat, 72Gil] observed an orthorhombic structure ("pseudotetragonal PbO") related to PbO-L that might correspond to a metastable distortion of the tetragonal lattice caused by an excess of oxygen. Another (metastable?) modification of PbO was suggested in the work of [39Leb] and [45Bys], but these findings have not been confirmed in later studies.

Composition Range of PbO-L and PbO-M. The oxygen content in PbO-L was found to reach up to $PbO_{1.1}$ by [32Leb], but later studies indicated that the solubility limit should be smaller. [45Bys] did not detect any changes in the lattice parameters for samples oxidized at various temperatures in air and 1 bar O_2, while [50Kat] found PbO-L to be able to dissolve oxygen up to a value of $PbO_{1.02}$. [54Gro] did not see any evidence in their data for a significant deviation from the ideal stoichiometry. [59And] observed that a composition of $PbO_{1.08}$ already lies in a two phase-field at 583 K, and [68Roo] observed the oxygen content to reach $PbO_{1.001}$ for samples in equilibrium with Pb_3O_4-T (Pb_3O_4, minium, red lead) at 723 K. This value of [68Roo] agrees well with the results of [67Nor], but the latter study could have been for PbO-L or PbO-M. There is no indication of a possible oxygen deficiency in PbO-L.

The oxygen content in PbO-M was also reported to reach up to $PbO_{1.1}$ by [32Leb], but no evidence for this deviation from the ideal stoichiometry could be detected in the later works [45Bys, 50Kat, 59And]. A deficiency in oxygen was observed from emf measurements at low oxygen partial pressure by [64And]. The composition of oxygen-deficient PbO-M may reach $PbO_{0.998}$ according to [73Eld]. More recently, the oxygen solubility in PbO-M was investigated by [79Kov] by a gas-volumetric method. The oxygen content was measured isothermally between 773 and 1023 K for oxygen partial pressures ranging from about 300 Pa to values not exceeding the PbO-M + Pb_3O_4-T equilibrium. Their results show an excess of oxygen in PbO-M that stays about constant with temperature for a given oxygen partial pressure. The solidus line of PbO-M was then derived using the oxygen partial pressure data on the PbO-M + Pb_3O_4-T equilibrium from [66Ott]. The values of the oxygen content in PbO-M determined by this method were in good agreement with results of chemical analysis [79Kha].

Thermodynamic Properties of PbO-L. The heat capacity of PbO-L has been measured by [58Kin] between 53 and 296

K, who derived a value of 65.3 J/mol · K for the entropy at 298 K. JANAF [85Cha] adopted the value of 66.3 J/mol · K, based on the analogy between the curves for PbO-L and PbO-M, by considering the difference observed for PbO-M between the extrapolation of [58Kin] below 53 K and the values measured by [60Kos]. Enthalpy increments have been measured by [42Spe] between 673 and 823 K. It is uncertain whether the PbO-L or PbO-M phase was measured in the earlier studies of the heat capacity by [1841Reg], [1865Kop], and [13Mag]. Heat capacity and enthalpy increments of PbO-L are shown in Fig. 1 and 2, respectively.

The difference in the enthalpies of formation of PbO-L and PbO-M at 298 K has been measured as 1648 ± 300 J/mol by [64Kna] using solution calorimetry. The energy of formation at 298 K has been derived from cell reactions by [23Smi] and [32Spe].

The data on Gibbs energy of formation, enthalpy of formation, and entropy at 298 K are in good agreement. These properties are listed for PbO-L as well as for the other stable lead oxides in Table 1.

PbO-L ↔ PbO-M Transformation. The transformation temperature between PbO-L and PbO-M has been studied by several authors, and large differences were observed as can be seen from Table 2. The largest discrepancies are certainly due to the very slow kinetics of the reaction. The conversion of PbO-L to PbO-M is more easily observed than the opposite. In one of the most extensive studies, [61Whi] characterized this transformation as straightforward. Nevertheless, in continuous heating of PbO-L, [68Cou] observed the transformation to extend between 763 and 873 K. The kinetics of the PbO-M to PbO-L conversion is much slower. PbO-M can be preserved for longer times well below the reported temperatures of the transformation; for example, [61Whi] did not observe any conversion in PbO-M samples maintained for 9 days at temperatures as low as 573 K.

As indicated by arrows in Table 2, most studies only observed the decomposition of PbO-L into PbO-M. The lowest temperatures reported for this reaction are in good agreement among each other around 762 K [34Coh, 41Pet, 46Kam, 46Pam, 68Cou]. The transformation temperature of PbO-M into PbO-L seems to have been observed with some reliability by [34Coh] and [61Whi] only. [34Coh] noted that the yellow to red transformation seen optically by [21Jae] (and possibly in earlier studies) probably corresponds to the formation of the red Pb_3O_4-T, as a similar study using XRD analysis indicated [24Koh]. The extrapolation from [61Whi] to ambient pressure gives a value of 816 K in agreement with the results of [36Ren1], [36Ren2], and [68Roo]. This reduces the uncertainty in the value of the transition temperature to an interval of about 50 K between the values of [34Coh] and [61Whi].

Other factors may affect the transformation temperature. [61Whi] showed that an increase of the total pressure increases the stability of PbO-M over PbO-L. The influence of the oxygen partial pressure has, however, not been definitively answered. Both PbO-L and PbO-M exhibit small ranges of solid solution, and the temperature of the transformation may thus be expected to vary with small changes in the oxygen content. On one hand, it could be expected that higher oxygen partial pressure would stabilize PbO-L over PbO-M because a larger oxygen content was found in PbO-L than in PbO-M [50Kat, 59And], because PbO oxidizes preferentially to higher oxides via the PbO-L modification [46Pam, 50Kat] and because traces of PbO-L have been observed in PbO-M specimens prepared at higher oxygen partial pressures but not in specimens prepared at lower ones [79Kov]. On the other hand, however, [68Roo] measured a decrease in the transformation temperature from 825 to 802 K as the oxygen content in PbO increased from 1.000 to 1.001.

Furthermore, the transformation may be affected by impurities as shown by [67Kwe]. They found that various elements, such as Si, could stabilize PbO-M over PbO-L. As mentioned by [68Roo], these impurity elements of valency larger than two could give rise to oxygen excess (or lead vacancies) and in this way increase the stability of PbO-M, if they dissolve preferentially in that modification.

In conclusion, it does not seem appropriate to recommend a single value because the transformation temperature should be probably considered as a function of the oxygen content. As PbO-L and PbO-M are approximated as stoichiometric compounds, the authors use the value of 762 K in agreement with many thermodynamic compilations, such as [85Cha], due to the excellent agreement found between several studies at this temperature and because this value is not excluded from the

Table 2 Temperature of the PbO-L ↔ PbO-M Transformation at 1 bar

Temperature, K	Method	Reference
853 (?)	...	[1897Lec]
893 (→)	Optical	[06Rue]
860 (→)	Optical	[21Jae]
762 (↔)	Optical	[34Coh]
803 (→)	Dilatomery	[36Ren1]
423 (←)	Optical	[39Leb]
823 (→)	DTA	[39Leb]
763 (→)	Optical	[41Pet]
759 to 762 (→)	Optical	[46Kam]
761 (?)	...	[46Pam]
816 (↔)	XRD	[61Whi]
763 (→)	HTXRD	[68Cou]
802 to 825 (→)	XRD	[68Roo]
762	Assessed	[85Cha]
813	Assessed	[88Wri]
762	Assessed	This work

HTXRD, high-temperature XRD.

Table 3 Enthalpy and Entropy of the PbO-L ↔ PbO-M Transformation

Temperature, K	ΔH, kJ/mol	ΔS, J/mol · K	Reference
298	240	...	[61Whi]
	1648	...	[64Kna]
	1613	2.39	This work
762	1027	1.35	This work
816	650	0.79	[61Whi]

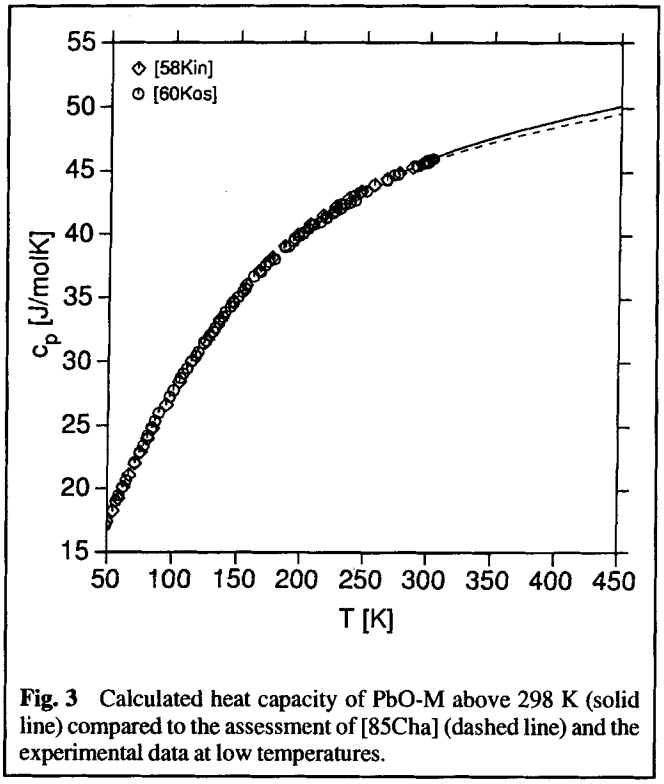

Fig. 3 Calculated heat capacity of PbO-M above 298 K (solid line) compared to the assessment of [85Cha] (dashed line) and the experimental data at low temperatures.

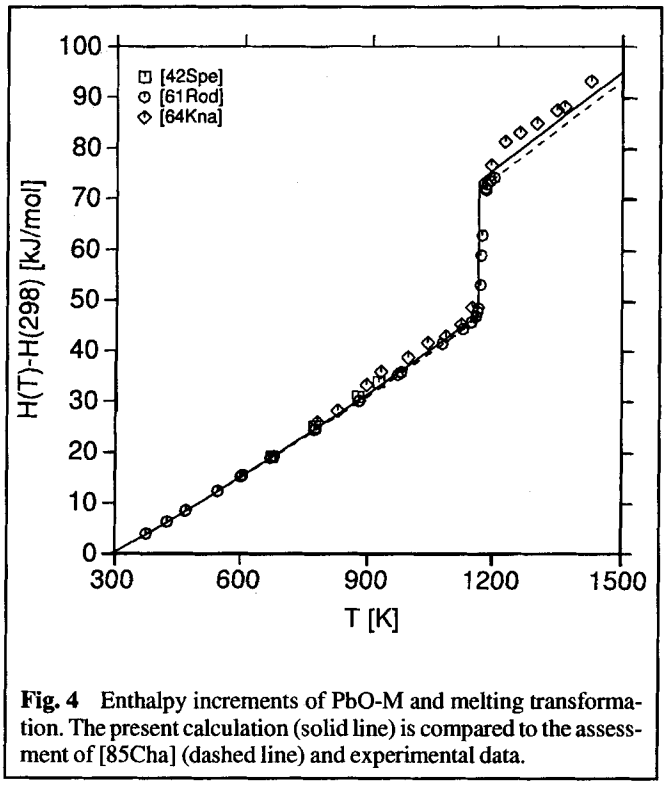

Fig. 4 Enthalpy increments of PbO-M and melting transformation. The present calculation (solid line) is compared to the assessment of [85Cha] (dashed line) and experimental data.

Table 4 Gibbs Energy of the Reaction Pb(L) + ½ O_2 = PbO-M

ΔG^0, J/mol	Temperature, K	emf cell	Crucible	Reference
–219 367 + 100.92 *T*	720 to 1070	Pb, PbO|MSZ|Ni,NiO	MSZ	[64Alc]
–218 059 + 98.20 *T*	773 to 1160	Pb, PbO|CSZ|Ni,NiO	CSZ	[64Mat1, 64Mat2]
–215 058 + 96.39 *T*	772 to 1160	Pb, PbO|CSZ|Ni,NiO	ThO_2	[68Cha]
–218 099 + 98.89 *T*	748 to 1130	Pb, PbO|CSZ|Ni,NiO	CSZ	[71Jac]
–215 058 + 96.23 *T*	1023 to 1170	Pb, PbO|CSZ|O_2	CSZ	[72Szw]
–214 095 + 94.14 *T*	993 to 1159	Pb, PbO|CSZ|Fe,FeO	Al_2O_3	[73Meh]
–214 660 + 95.65 *T*	865 to 1159	Pb, PbO|CSZ|?	CSZ	[75Cal]
–215 000 + 97.28 *T*	923 to 1152	Pb,PbO|CSZ|Ni,NiO	CSZ	[75Iwa, 78Iwa]
–218 279 + 97.49 *T*	1008 to 1159	Pb,PbO|CSZ|Fe,FeO	Al_2O_3	[75Meh]
–216 606 + 98.03 *T*	1023 to 1143	Pb,PbO|CSZ|O_2	CSZ	[76Cha]
–215 231 + 96.54 *T*	1073 to 1145	Pb,PbO|CSZ|O_2	CSZ	[79Tas]
–216 000 + 97.4 *T*	623 to 1160	Pb,PbO|CSZ or YSZ|O_2	CSZ or YSZ	[80Sug]
–220 010 + 100.91 *T*	645 to 977	Pb,PbO|YSZ|O_2	Cr + Al_2O_3	[84Ban]
–212 640 + 92.54 *T*	767 to 901	Pb,PbO|CSZ|O_2	Graphite	[95Mal]

MSZ, ZrO_2(+MgO); CSZ, ZrO_2(+CaO); YSZ, ZrO_2(+Y_2O_3).

uncertainty range of [61Whi]. It should be also noted that the data of [61Whi] led to a value for the enthalpy of transition diverging from the calorimetric study of [64Kna]. Nevertheless, because crucible materials such as glass, porcelain, and so forth, have been used in many of the studies leading to 762 K, it cannot be excluded that this value might correspond to the transformation temperature of Si-saturated PbO. The higher value of 813 K was preferred in the review of [88Wri].

Values for the enthalpy of transition have been derived from data at higher pressures using the Clapeyron relation [61Whi] and from the difference in the heat of dissolution in nitric acid [64Kna]. The data are presented in Table 3.

Thermodynamic Properties of PbO-M. The heat capacity of PbO-M has been measured by [58Kin] from 54 to 296 K and by [60Kos] from 12 to 303 K. Enthalpy increments have been measured by [42Spe], [64Kna], and [61Rod]. Heat capacity and enthalpy increments of PbO-M are shown in Fig. 3 and 4, respectively. The data of [42Spe] cover a smaller temperature range, and those of [64Kna] show more scatter. The data of [61Rod] were then favored in the JANAF assessment [85Cha], even though the authors expressed some reservation on the purity of their material and obtained a slightly higher melting point for PbO-M than usually accepted. Here all data are considered equally reliable.

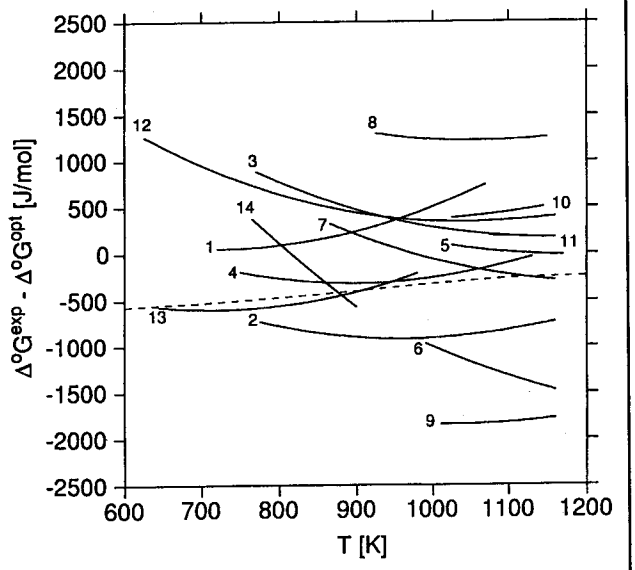

Fig. 5 Difference between the experimental and the presently calculated Gibbs energy of the reaction Pb + ½ O_2 = PbO-M. Experimental data are from: 1 [64Alc], 2 [64Mat], 3 [68Cha], 4 [71Jac], 5 [72Szw], 6 [73Meh], 7 [75Cal], 8 [75Iwa, 78Iwa], 9 [75Meh], 10 [76Cha], 11 [79Tas], 12 [80Sug], 13 [84Ban], 14 [95Mal]. The JANAF values [85Cha] are indicated by a dashed line.

The enthalpy of formation of PbO-M has been determined by reaction calorimetry from the reduction by hydrogen gas [70Esp]. The Gibbs energy of formation of PbO-M has been derived from numerous emf studies at 298 K [32Spe] and at higher temperatures [64Alc, 64Mat1, 64Mat2, 68Cha, 71Jac, 72Szw, 73Meh, 75Cal, 75Iwa, 78Iwa, 75Meh, 76Cha, 79Tas, 80Sug, 84Ban, 95Mal]. The thermodynamic properties at 298 K are shown in Table 1, and the higher temperature results are listed in Table 4 and plotted in Fig. 5. All data are in close agreement.

Melting of PbO-M. Experimental determinations of the melting point of PbO-M are summarized in Table 5. The early data [08Sch, 09Coo, 09Hil, 12Kro, 21Jae, 22Bel, 34Gel, 36Kra] have been assessed by [63Sch], who adopted the value of 1159 K from [34Gel] and [36Kra]. The results of [34Coh] and [64Kna] are consistent with this analysis. [81Kha] measured a constant value slightly higher than the monotectic temperature at lower oxygen pressures. The somewhat higher value of [61Rod] may be discarded on account of the doubt expressed by the authors themselves concerning the purity of the material. Except for [1897Lec] all data lie more or less between 1143 and 1159 K, which probably covers the temperature range of the L_2 + PbO-M liquidus from the monotectic temperature (1143 K) to the congruent melting point of PbO-M (1159 K). The monotectic reaction is discussed below.

The enthalpy of melting has been obtained from calorimetric data [61Rod, 64Kna, 71War], from the change in slope of emf measurements [64Mat, 68Cha, 71Jac, 72Szw, 73Meh, 75Cal, 75Iwa, 75Meh, 76Cha, 78Iwa, 79Tas], and from the

Table 5 Melting Temperature of PbO-M

Temperature, K	Reference
1103	[1897Lec]
1152	[08Sch]
1161	[09Coo]
1149	[09Hil]
1161	[12Kro]
1150 to 1152	[21Jae]
1143	[22Bel]
1157	[34Coh]
1159	[34Gel]
1159	[36Kra]
1159	[39Leb]
1170	[61Rod]
1159	[63Sch]
1158	[64Kna]
1143	[81Kha]
1159	This work

Table 6 Enthalpy and Entropy of Melting of PbO-M

ΔH, kJ/mol	ΔS, J/mol · K	Method	Reference
22.5 to 24.3	...	Liquidus	[55Ric](a)
29.3	25.1	Liquidus	[55Ric]
25.6	21.9	Calorimetry	[61Rod]
27.6	...	Calorimetry	[64Kna]
26.8	23.6	emf	[64Mat1, 64Mat2]
24.4	21.2	emf	[68Cha]
27.1	24.0	emf	[71Jac]
26.8	...	Calorimetry	[71War]
25.5	21.3	emf	[72Szw]
28.9	24.7	emf	[73Meh]
28.8	24.3	emf	[75Cal]
30.3	26.4	emf	[75Iwa, 78Iwa]
28.9	24.9	emf	[75Meh]
28.0	24.5	emf	[76Cha]
25.4	22.2	emf	[79Tas]
26.5	22.9	Assessed	This work

(a) [55Ric] analysis of earlier data on melting-point depression.

melting point depression in various systems [55Ric]. These values are listed in Table 6. Practically all data are within in the range 27 ± 3 kJ/mol. Here, calorimetric studies of equal reliability are considered and a value of 26.6 ± 1 kJ/mol is favored.

Thermodynamic Properties of Liquid PbO. The heat capacity of the oxide liquid L_2 can be derived from the enthalpy increment data of [61Rod, 64Kna]. Both studies are in close agreement and lead to a value of about 65 J/mol · K. The Gibbs energy of the reaction Pb(L) + ½O_2 = PbO(liq) has been derived from numerous measurements of the oxygen potential in the miscibility gap using emf cells [59Del, 60Kvy1, 60Kvy2, 63Min, 64Mat1, 64Mat2, 67Sri, 68Cha, 71Jac, 71Kap, 72Cod, 72Szw, 73Kap, 73Meh, 75Cal, 75Iwa, 75Meh, 76Cha, 76Leu, 76Per, 76Sui, 77Sug, 78Iwa, 79Tas] and by reduction with C

Table 7 Gibbs Energy of the Reaction Pb(L) + ½ O_2 = PbO(liq)

ΔG^0, J/mol	Temperature, K	emf cell	Crucible	Reference
-191 093 + 79.89 *T*	1073 to 1473	Pb|PbO|O_2	?	[63Min]
-191 229 + 74.56 *T*	1160 to 1423	Pb,PbO|CSZ|Ni,NiO	CSZ	[64Mat1, 64Mat2]
-191 753 + 79.08 *T*	1173 to 1353	Pb|PbO|O_2	Al_2O_3	[67Sri]
-190 623 + 75.15 *T*	1160 to 1371	Pb,PbO|CSZ|Ni,NiO	ThO_2	[68Cha]
-191 008 + 74.91 *T*	1130 to 1423	Pb|PbO|CSZ|Ni,NiO	CSZ	[71Jac]
-180 761 + 65.44 *T*	1165 to 1313	Pb,PbO|CSZ|O_2	Al_2O_3	[71Kap]
-214 430 + 91.14 *T*	1150 to 1250	Pb|PbO|O_2	?	[72Cod]
-190 623 + 74.89 *T*	1170 to 1353	Pb,PbO|CSZ|O_2	CSZ	[72Szw]
-191 209 + 73.64 *T*	1165 to 1315	Pb,PbO|CSZ|O_2	Al_2O_3	[73Kap]
-185 226 + 69.45 *T*	993 to 1273	Pb,PbO|CSZ|Fe,FeO	Al_2O_3	[73Meh]
-185 891 + 71.38 *T*	1159 to 1445	Pb,PbO|CSZ| ?	CSZ	[75Cal]
-184 700 + 70.92 *T*	1152 to 1323	Pb,PbO|CSZ|Ni,NiO	CSZ	[75Iwa]
-189 410 + 72.63 *T*	1159 to 1273	Pb,PbO|CSZ|Fe,FeO	Al_2O_3	[75Meh]
-188 615 + 73.56 *T*	1143 to 1343	Pb,PbO|CSZ|O_2	CSZ	[76Cha]
-189 037 + 73.70 *T*	1176 to 1373	Pb,PbO|CSZ|O_2	CSZ	[76Leu]
-214 430 + 94.14 *T*	1173 to 1373	Pb|PbO|O_2	?	[76Per]
-194 472 + 81.30 *T*	1163 to 1293	Pb|PbO|O_2	Al_2O_3	[76Sui]
-191 350 + 74.60 *T*	1249 to 1336	Pb,PbO|CSZ|Ni,NiO	Al_2O_3	[77Sug]
-189 851 + 74.36 *T*	1145 to 1203	Pb,PbO|CSZ|O_2	CSZ	[79Tas]

MSZ, ZrO_2(+ MgO); CSZ, ZRO_2(+ CaO).

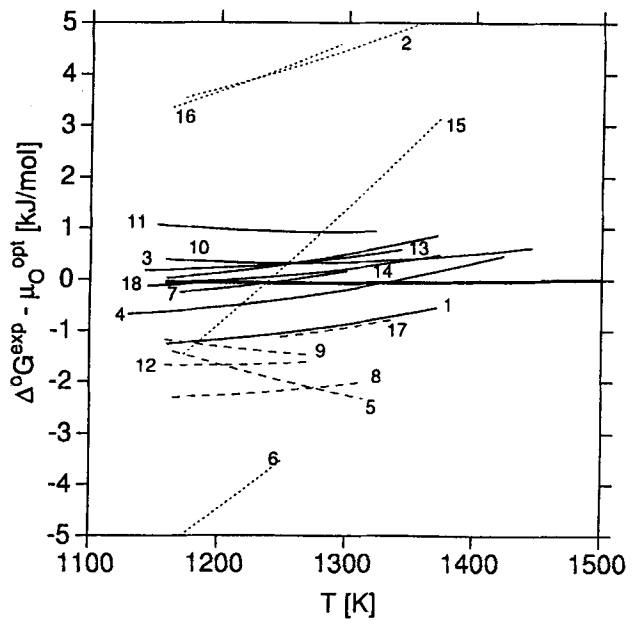

Fig. 6 Difference between the calculated oxygen potential in the miscibility gap and the measured values that are commonly taken as equal to the Gibbs energy of the reaction Pb + ½ O_2 = PbO(liq). The calculated Gibbs energy of this reaction is shown by a thick line. Experimental data are from: 1 [63Min], 2 [64Mat1, 64Mat2], 3 [67Sri], 4 [68Cha], 5 [71Jac], 6 [71Kap], 7 [72Cod], 8 [72Szw], 9 [73Kap], 10 [73Meh], 11 [75Cal], 12 [75Iwa, 78Iwa], 13 [75Meh], 14 [76Cha], 15 [76Leu], 16 [76Per], 17 [76Sui], 18 [77Sug], and 19 [79Tas]. Solid lines indicate measurements combining solid electrolyte and ZrO_2 or ThO_2 crucible; dashed lines indicate measurements combining solid electrolyte and Al_2O_3 crucible; dotted lines indicate the use of liquid electrolyte.

and [60Kvy1, 60Kvy2]. These results are summarized in Table 7 and plotted in Fig. 6. The three points of [59Del] and the scattered data of [60Kvy1] and [60Kvy2] are omitted from Fig. 6. The Gibbs energy of the reaction can be calculated from the measured oxygen potential if the values for the activity of Pb(L) and PbO(liq) are known. This calculation is usually simplified by assuming that $a_{PbO} \equiv a_{Pb}$, which is a reasonable approximation at least below 1373 K, according to the estimation of [79Tas].

The discrepancies among the data have been discussed by [79Tas], who pointed out two sources of systematic errors. Firstly, data obtained using an alumina crucible should be discarded as alumina decreases the activity of lead oxide leading to too negative values. Secondly, data obtained using a liquid electrolyte should not be considered because the conductivity of the electrolyte is not purely ionic. The agreement among the results combining the solid electrolyte and ZrO_2 or ThO_2 crucible was good.

2.2 The Pb-PbO Range

The only stable crystal structure of Pb at ambient pressure is fcc. There are no reports about the oxygen saturation limit in solid Pb, and it is certainly extremely small as it could never be detected [76Rei]. At pressures higher than 10.3 GPa, cph Pb (εPb) is reported stable [83Kin], but the transformation point is unknown. Metastable εPb could be obtained at ambient pressure by splat quenching of liquid Pb [79Akh]. Early reports about solid compounds between Pb and PbO have not been substantiated in later studies. See [69Han] and [88Wri] for a review of these investigations. The Pb-PbO range is characterized by a large miscibility gap in the liquid phase.

Oxygen Solubility Limit and Thermodynamics of L_1. The oxygen solubility in the Pb-rich liquid (L_1) has been investigated in numerous studies, beginning with the work of

[1892Lun]. The solubility limit has been determined using sampling techniques [1892Lun, 30Bre, 38Wer, 39Bak, 40Wor, 44Gro, 52Bar, 52Fis, 53San, 54Geb, 55Bar, 76Kry, 74Kux, 76Rei, 75Kry, 76Ise, 82Ste], using vapor equilibration techniques [53Dan, 55Ric], using measurements of surface tension [59Bra], and using electrochemical measurements [64Alc, 71Jac, 72Szw, 76Cha, 77Ise, 79Tas, 84Con]. All these data are presented in Fig.7.

The spread in the data is large and reflects the experimental difficulties. In sampling techniques, a large uncertainty is due to the possible inclusion of Pb or impurity oxides in the analysis of the oxygen content. The phase separation between the lead oxide and L_1 is particularly slow due to the small difference in density so that oxide precipitates are not easily removed. Thus, the lowest values of the oxygen content measured in the lower temperature range have been favored in the recent discussions [76Kry, 76Rei, 75Kry, 82Ste, 88Wri]. These values are also in good agreement with extrapolations from the higher-temperature range based on vapor equilibration and emf data [55Ric, 64Alc, 79Tas]. Some of the recent studies at low temperatures are nevertheless in disagreement [78Car, 82Zau, 84Con].

At higher temperatures, it has been argued that a sampling technique is no longer reliable because the demixing of L_1 and L_2 occurs before the high-temperature equilibrium can be frozen upon quenching [53Dan]. [53Dan] and [55Ric] preferred, therefore, to derive the solubility limit by extrapolation from activity data from the PbO-SiO_2 system. Higher solubility values were obtained by [76Ise] and [77Ise] using both a sampling technique and emf measurements, while lower values were reported by [72Szw] and [74Kux]. At the intermediate temperatures, the data of [59Bra], [64Alc], [74Kux], and [79Tas], which were obtained from three different experimental methods, are relatively close to each other and should be considered much more reliable than the early sampling data [39Bak, 52Bar, 53San].

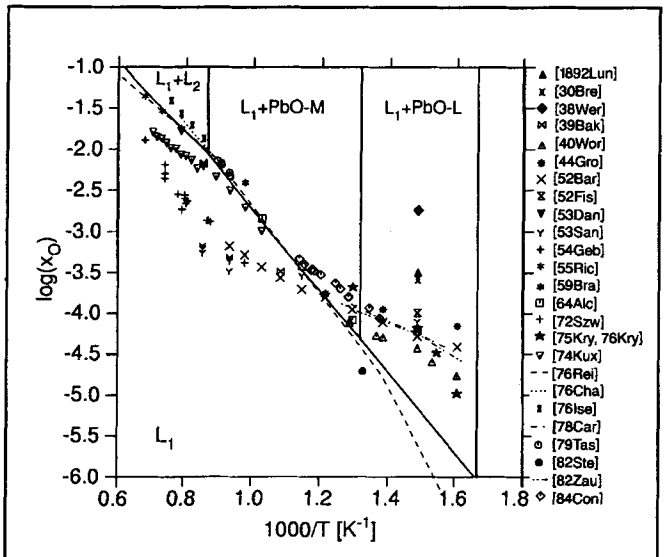

Fig. 7 Solubility of oxygen in the Pb-rich liquid (L_1).

The activity of oxygen in L_1 has been studied by several authors [76Cha, 77Ise, 79Ots, 79Tas, 81Ots] using emf measurements. The values for the activity coefficient derived from these investigations are plotted in Fig. 8. The results of [76Cha] and [77Ise] show a larger change in the activity coefficient as a function of the concentration than observed by

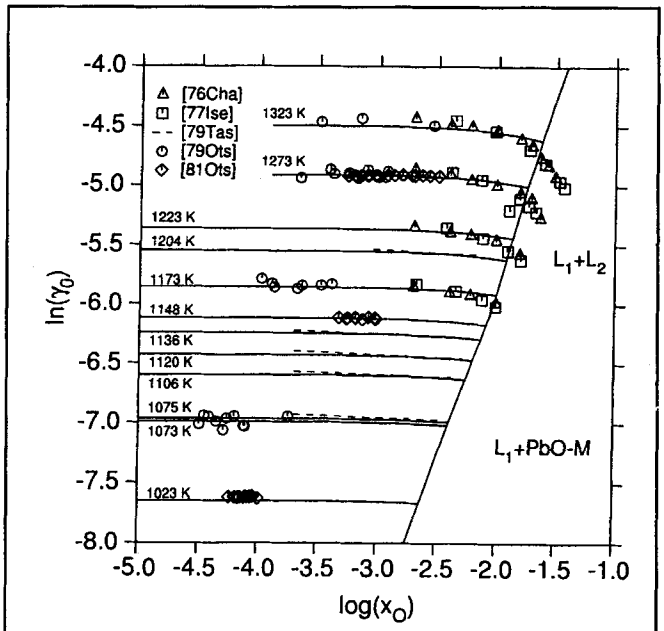

Fig. 8 Oxygen activity coefficient in the Pb-rich liquid (L_1). Calculated solid lines are compared with experimental data at a few selected temperatures covering the range of measurements.

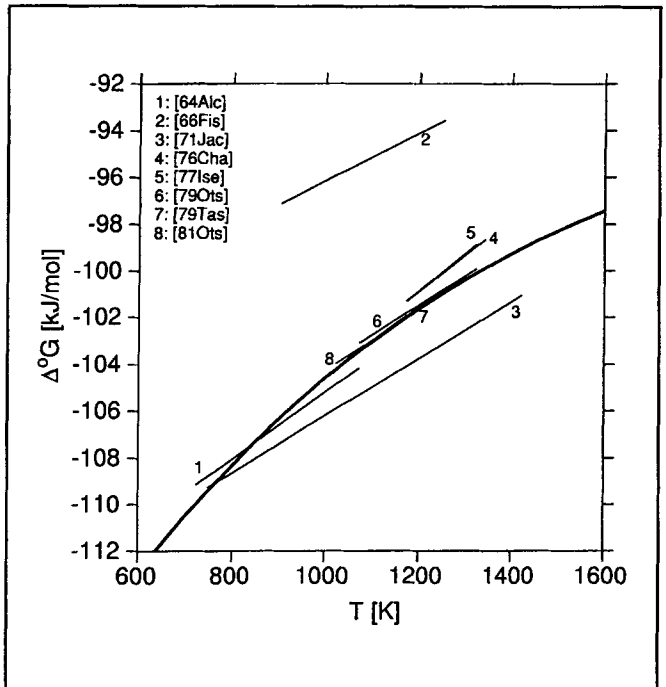

Fig. 9 Gibbs energy of dissolution of gaseous oxygen in liquid Pb at infinite dilution using 1 bar O_2 gas and a 1 at.% standard state as reference.

Table 8 Invariant Points of the Pb-O system

Equilibrium	Temperature, K	p_{O_2}, bar	$X_O(L_1)$	$X_O(L_2)$	Reference
$L_1 = Pb + PbO\text{-}L$	600	...	0.8×10^{-6}	...	[55Ric]
	600	...	60×10^{-6}	...	[74Kux]
	600	...	0.5×10^{-6}	...	[76Rei]
	600	...	10^{-6}	...	[88Wri]
	600.6	2.1×10^{-28}	0.95×10^{-6}	...	This work
$L_2 = L_1 + PbO\text{-}M$	1159(a)	...	0.0095	...	[55Ric]
	1159(a)	...	0.00896	...	[64Alc]
	1170(a)	...	0.0015	...	[72Szw]
	1146	...	0.00515	0.499	[74Kux]
	1143	...	0.0089	...	[76Cha]
	1143	...	0.0089	0.499	[77Ise]
	1145	...	0.0084	...	[79Tas]
	1142	...	...	...	[81Kha]
	1145	...	0.0085	...	[88Wri]
	1157	4.3×10^{-10}	0.009	0.499	This work
$L = L_1 + L_2$	1583	...	0.28	0.28	[77Ise]
	1807	3×10^{-4}	0.296	0.296	This work
$L_2 + PbO\text{-}M + Pb_3O_4\text{-}T$	1148	124	...	...	[64Whi, 65Roy]
	1159	167	...	0.5	This work
$Pb_{12}O_{17} = Pb_3O_4\text{-}T + Pb_{12}O_{19}$	653	2	...	...	[64Whi, 65Roy]
	662	4.2	...	...	This work

(a) Taken as equal to the melting point of PbO-M.

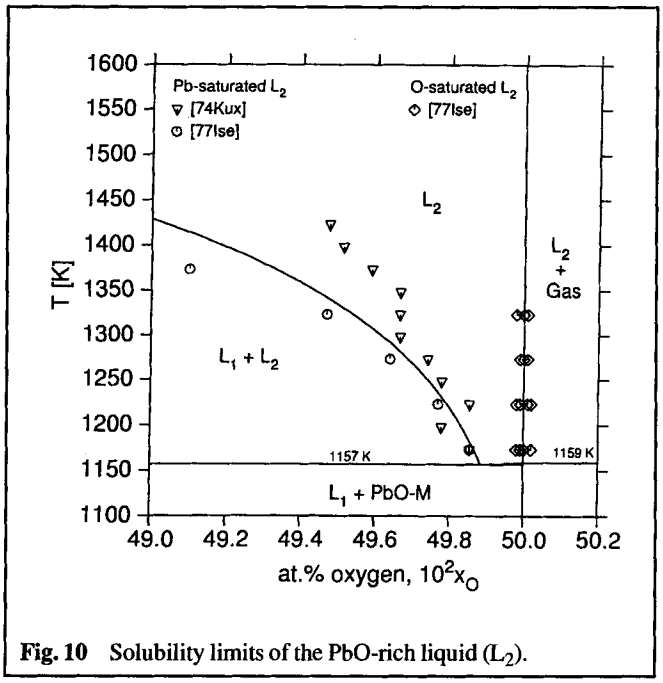

Fig. 10 Solubility limits of the PbO-rich liquid (L_2).

[79Ots], [79Tas], and [81Ots], but the agreement among all data is rather good at lower oxygen concentration where the data of [76Cha] and [77Ise] approach the activity coefficients of [79Ots]. At higher oxygen concentrations close to the saturation limit, the uncertainty in the activity data increases, partly because large changes in concentration cause only small changes in the emf. The functions for the Gibbs energy of dissolution of gaseous oxygen in L_1 derived from these studies are shown together with the other data from [64Alc], [66Fis], [71Jac], and [72Szw] in Fig. 9.

Solubility Limits and Thermodynamics of L_2. The composition of the lead-saturated PbO liquid (L_2) has been measured by [74Kux] and [77Ise]. These data are in agreement close to the monotectic temperature and deviate from each other above 1250 K, as can be seen in Fig. 10. The reported monotectic temperatures are listed in Table 8.

The composition of the oxygen-saturated L_2 can probably exceed 50 at.% O, but conclusive data are lacking. [54Hof] observed a eutectic structure forming upon solidification of liquid PbO under an oxygen stream. They did not identify the other solid phase besides PbO-M and mentioned, without giving data, that they determined an excess of oxygen in L_2 that exceeded the experimental uncertainty. [64Whi] and [65Roy] reported the eutectic reaction $L_2 = PbO\text{-}M + Pb_3O_4\text{-}T$ at 1149 K and a pressure corresponding to 124 bar O_2. The uncertainty in the temperature of this reaction is, however, comparable to the size of the observed melting point depression, and no data were given regarding the composition of L_2. [74Sas] estimated the change in the oxygen concentration of L_2 between an argon atmosphere (10^{-6} to 10^{-4} bar O_2) and 1 bar O_2 from permeability and diffusion measurements, and [77Gra] determined volumetrically the solubility of oxygen as function of the oxygen partial pressure at 1173 K. However, in both cases, this does not allow a conclusion to be drawn as to the absolute value of the oxygen content. Finally, [77Ise] studied the composition of oxygen-

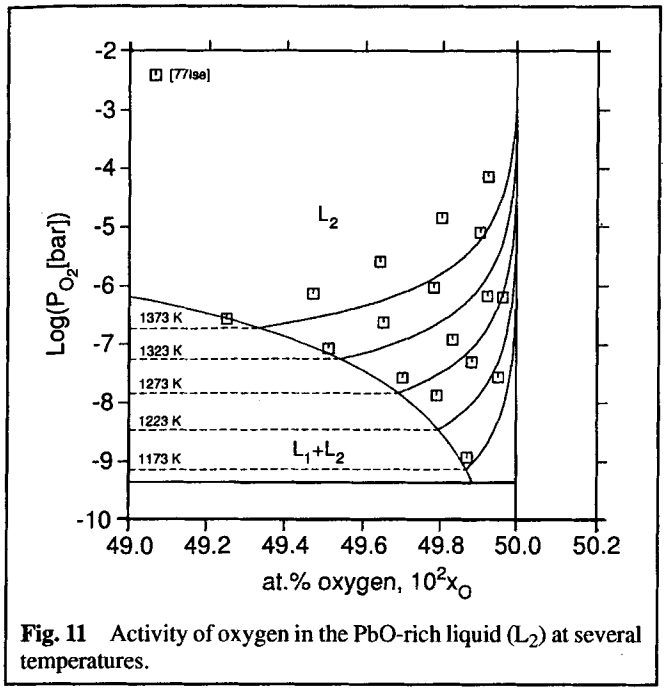

Fig. 11 Activity of oxygen in the PbO-rich liquid (L_2) at several temperatures.

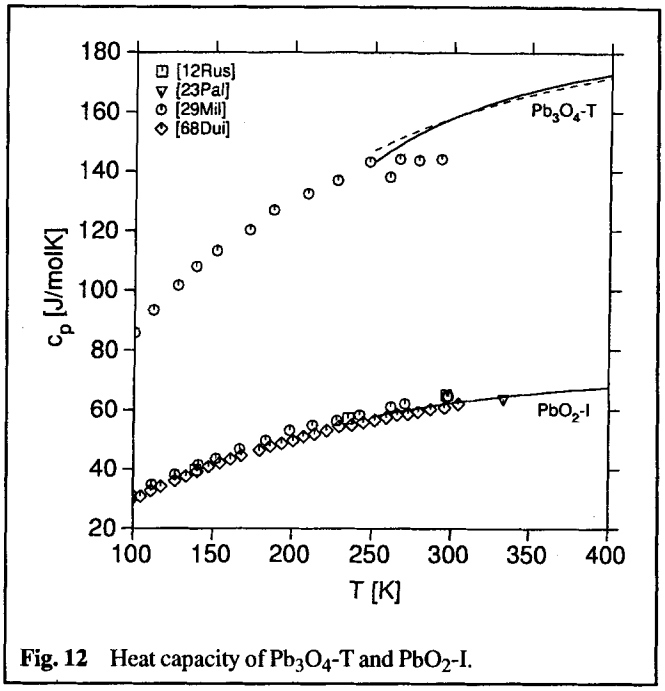

Fig. 12 Heat capacity of Pb_3O_4-T and PbO_2-I.

saturated L_2 by thermogravimetric measurements in the temperature range 1173 to 1323 K within the oxygen partial pressure range 0.027 to 1 bar O_2 and did not observe any significant deviation from the PbO composition.

The oxygen activity in L_2 has been measured between 1173 and 1373 K by [77Ise] using an emf cell. These data are shown in Fig. 11.

2.3 The PbO-PbO_2 Range

Stable and Other Phases. Two stable phases have been found at the Pb_3O_4 composition. Tetragonal Pb_3O_4-T is the stable form at ambient temperature and above. A phase transformation from Pb_3O_4-T into the orthorhombic Pb_3O_4-R was observed at 160 K by [72Gar]. The transformation temperature was later set at 170 K with the publication of additional data [78Gar, 78Gav]. [50Kat] and [72Gil] reported another orthorhombic structure ("pseudo-tetragonal Pb_3O_4"), not related to Pb_3O_4-R, to account for some abnormalities observed in the XRD pattern of Pb_3O_4-T [43Gro, 45Bys, 50Kat]. As for pseudotetragonal PbO, this might correspond to a metastable distortion of the tetragonal lattice caused by a deviation from the ideal stoichiometry.

Three stable phases have been found at the PbO_2 composition. Tetragonal PbO_2-I (βPbO_2, plattnerite) is the stable form at low temperatures and low pressures. PbO_2-I has, however, never been obtained from the direct oxidation of lower lead oxides, and there is some concern that it may not be a phase of the binary system because some small amounts of hydrogen have always been detected in PbO_2-I samples. More details on this aspect are given in [88Wri]. Two other modifications are stable at high pressure: orthorhombic PbO_2-II (Pb_8O_{15} [50Kat], αPbO_2 [50Zas]), and cubic PbO_2-III [68Syo]. The phase boundary between PbO_2-I and PbO_2-II has been studied by [56Bod, 61Whi, 64Whi, 65Kir, 65Roy, 82Hil], as has the one between PbO_2-II and PbO_2-III by [68Syo]. PbO_2-II can be obtained electrolytically at ambient temperature and pressure [50Zas].

Three phases may be considered stable between the composition Pb_3O_4 and PbO_2 [88Wri]. Two of them, $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$, are products of the decomposition of PbO_2 or the oxidation of PbO compounds, which have been observed in many studies but reported using various formulas. The third one is the monoclinic compound Pb_2O_3, which has been observed at high pressure [41Gro] and whose stability limits have been investigated by [64Whi] and [65Roy]. The identification of phases in the PbO-PbO_2 system is very closely related to the accuracy of the structural analysis because very similar XRD patterns are observed. Most structures appear to be related to the fluorite type, and small structural variations may arise through the arrangement of oxygen vacancies. The formulas $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$ were introduced by [59And] and correspond to two structures where the ordering of oxygen vacancies takes place. The formulas βPbO_x [45Bys] and Pb_9O_{13} [66Ott] have also been proposed for $Pb_{12}O_{17}$, and Pb_2O_3 [1878Deb], Pb_5O_8 [12Fis], Pb_7O_{11} [37Hol, 38Bar], αPbO_x [45Bys], Pb_9O_{14} [66Ott], and $PbO_{1.57}$ [69Bou] for $Pb_{12}O_{19}$. $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$ might also exhibit various modifications according to [72Gil], but further information is lacking.

The formation of solid solutions during the oxidation of PbO was observed in several early investigations [14Rei, 32Leb, 40Hol, 41Cla]. [50Kat] reported a broad solid-solution PbO_n to extend between Pb_3O_4 and $Pb_{12}O_{19}$. The structural characteristics of this disordered phase change among the ordered structures Pb_3O_4-T, $Pb_{12}O_{17}$, and $Pb_{12}O_{19}$ so that the solid solution has been characterized in two different intervals in the more recent studies. A solid solution exhibiting a hexagonal structure was described by [73Sor] between Pb_3O_4 and $Pb_{12}O_{17}$, whereas a pseudocubic one is known between $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$ ($PbO_{1.40\text{-}1.52}$ [59And], $PbO_{1.41\text{-}}$

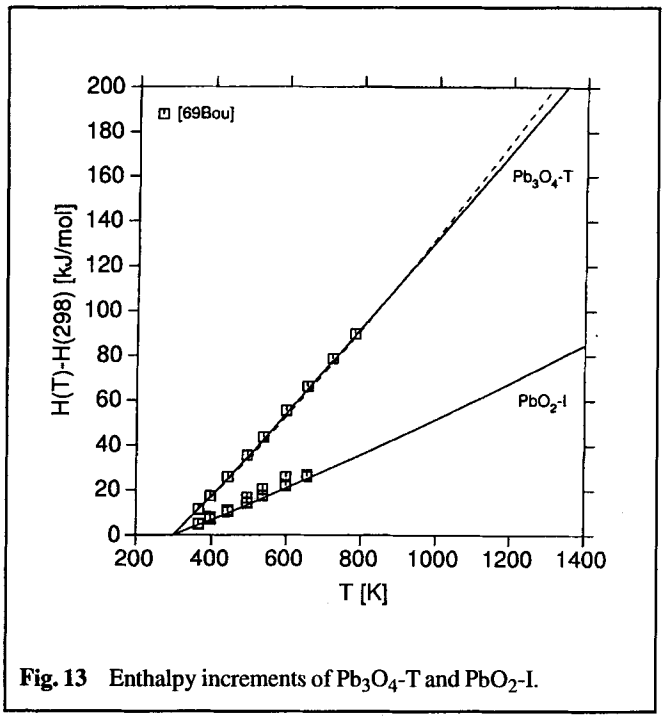

Fig. 13 Enthalpy increments of Pb_3O_4-T and PbO_2-I.

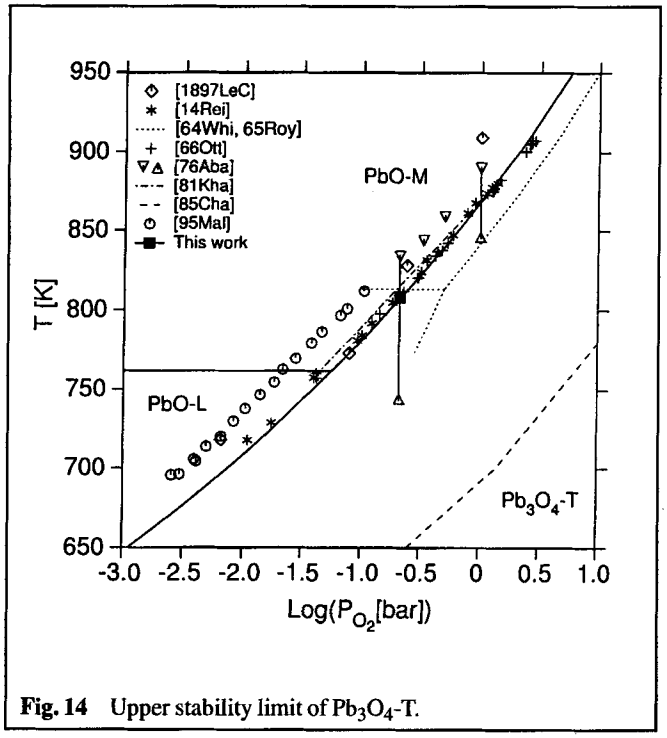

Fig. 14 Upper stability limit of Pb_3O_4-T.

$_{1.56}$ [73Sor]). These solid solutions are metastable [59And, 73Sor].

Composition and Thermodynamics of Pb_3O_4-T. The composition of Pb_3O_4-T has not been reported to vary significantly from the ideal stoichiometry. [45Bys] measured only slight changes in the oxygen content of Pb_3O_4-T samples prepared between 673 and 843 K from the oxidation of PbO and the decomposition of PbO_2. He did not observe any change in the lattice parameters.

The heat capacity of Pb_3O_4-T has been measured by [29Mil] between 71 and 293 K, and enthalpy increments have been determined by [69Bou] between 365 and 781 K. These data are shown in Fig. 12 and 13, respectively. [29Mil] did not report any anomaly at the temperature where the Pb_3O_4-R ↔ Pb_3O_4-T transformation was later found.

The enthalpy of formation at 298 K has been determined by [70Esp] as −718.7 ± 6.3 kJ/mol. Unfortunately, their sample was not free of impurity. They assumed the sample to consist of 90.1 mol% of Pb_3O_4-T and 9.9 mol% PbO based on the analysis of the Pb^{4+} content and corrected their result accordingly. The value of [70Esp] is compatible with the Gibbs energy of formation data from the cell reaction study of [34And]. However a much lower value for the Gibbs energy of formation was derived from the more recent electrochemical investigation of [63Cha].

The Pb_3O_4-T ↔ PbO-M Transformation. The transformation between PbO-M and Pb_3O_4-T has been investigated using equilibrium pressure measurements [1897LeC, 14Rei, 66Ott, 81Kha], thermal analysis [56But, 76Aba, 81Kha], XRD analysis of annealed samples [56But, 64Whi, 65Roy], and emf measurements [95Mal]. These data show some discrepancies among each other, but are all in much larger contradiction with the transformation temperatures calculated using the measured values of the entropy and enthalpy at 298 K [85Cha], as shown in Fig. 14.

The decomposition temperature of Pb_3O_4-T into PbO-M is calculated at 690 K in 1 bar O_2 [85Cha]. This value is definitively too low when one consider that PbO-M can be regularly oxidized to Pb_3O_4-T at much higher temperatures as was already shown by [1832Dum]. This contradiction indicates that some major uncertainty lies in the thermodynamic properties of Pb_3O_4-T at 298 K rather than in the data on the PbO-M ↔ Pb_3O_4-T transformation. The uncertainty in the transformation temperature is better expressed through the hysteresis observed in thermal analysis runs [66Ott, 76Aba] and indicated by experimental error bars in Fig. 14 and through the general scatter of the data obtained by several experimental methods.

In order to determine more precisely the temperature of this transformation, the authors decided to perform the following complementary experimental investigation. Pelletized samples of starting material PbO-M (Wako Ltd., 99% purity) and Pb_3O_4-T (Aldrich Co. Inc., 99% purity) were placed in two rows on an alumina crucible in the temperature gradient range of the furnace. The samples were annealed in air for 52, 187, and 636 ks, and after annealing the phase constitution was determined using powder XRD analysis. Formation of the PbO-M phase in the Pb_3O_4-T samples was detectable above 815.1 K after 52 ks, above 811.1 K after 187 ks, and above 809.4 K after 636 ks. The temperature limit for the formation of Pb_3O_4-T in PbO-M samples increased slowly with time and reached 806.8 K after 636 ks. Patterns of the XRD analysis after 636 ks are shown in Fig. 15. The value of the transformation temperature between PbO-M and Pb_3O_4-T in air is thus narrowed to the interval 806.8 to 809.4 K, and the average value 808 ± 2 K is adopted here.

This result is in good agreement with the previous works of [14Rei, 66Ott, 81Kha]. The authors consider these data to represent best the equilibrium state and adopt the equilibrium

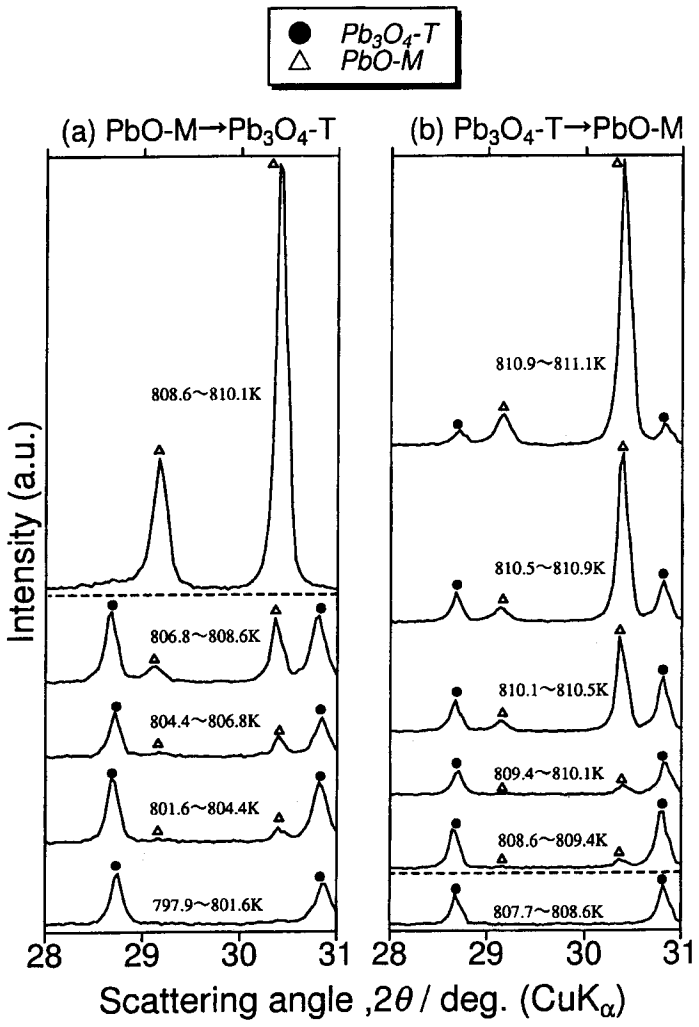

Fig. 15 Powder XRD profiles of the samples sintered for 636 ks. The dashed lines represent the observed temperature limits for the formation of **(a)** Pb_3O_4-T and **(b)** PbO-M.

pressure versus temperature values from [14Rei], [66Ott], and [81Kha]. The phase boundary given by [64Whi] and [65Roy], is subject to a larger uncertainty due to the limited number of samples covering a wide range of temperatures and pressures, but should be considered for the high-pressure range. The results of [95Mal] fall on a line with those of [76Aba]. As the latter correspond to the upper limit of the hysteresis obtained in thermal analysis runs, both sets of data are, therefore, expected to overestimate the equilibrium values.

Composition and Thermodynamics of $Pb_{12}O_{17}$, $Pb_{12}O_{19}$, and PbO_2-I. Both $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$ probably have a very narrow composition range. The composition range of $Pb_{12}O_{17}$ (=$PbO_{1.417}$) has been given as $PbO_{1.47\text{-}1.51}$ [45Bys], $PbO_{1.42\text{-}1.50}$ [56But], and $PbO_{1.41\text{-}1.42}$ [59And]. The latter values are considered the more reliable [88Wri], and thus the effective oxygen content in $Pb_{12}O_{17}$ is very close to the formula adopted from crystallographic considerations. The composition range of $Pb_{12}O_{19}$ (=$PbO_{1.583}$) has been given as $PbO_{1.50\text{-}1.66}$ [45Bys], $PbO_{1.566\text{-}1.571}$ [56But], and $PbO_{1.57}$ [37Hol, 59And]. It is thus improbable that the composition of $Pb_{12}O_{19}$ deviates significantly from $PbO_{1.57}$. The crystallography-based formula $Pb_{12}O_{19}$ corresponds to a slightly higher oxygen content of $PbO_{1.583}$.

PbO_2-I can tolerate some oxygen deficiency. X-ray diffraction patterns of a second phase in PbO_2-I samples have been detected at the oxygen content of $PbO_{1.92}$ [45Bys], $PbO_{1.935}$ [56But], and $PbO_{1.938}$ [59And], and thus the composition limit of PbO_2-I was estimated as $PbO_{1.95}$ [45Bys, 56But] and $PbO_{1.96}$ [59And]. In other investigations, lower values such as $PbO_{1.66}$ [32Leb] and $PbO_{1.875}$ [50Kat] had also been reported. The ideal composition PbO_2 has never been observed in any samples.

Enthalpy increments have been measured for $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$ between 365 and 722 K by [69Bou]. The data are shown in Fig. 16. The energy of formation of $Pb_{12}O_{19}$ at 298 K has been determined by [63Cha] from the cell reaction $Pb_{12}O_{19} + 5H_2O = 12PbO_2\text{-I} + 5H_2$.

Heat capacity and enthalpy increments of PbO_2-I are shown in Fig. 12 and 13, respectively. The heat capacity of PbO_2-I was measured by [29Mil] between 70 and 297 K, and by [68Dui] between 15 and 318 K. The data of [29Mil] led to the value of 76.4 J/mol · K for the entropy at 298 K, whereas [68Dui] obtained the value 71.8 J/mol · K. The earlier measurement of the heat capacity by [12Rus] agree closely with the data of [29Mil], while the value of [23Pal] is in good agreement with the data of [68Due]. [69Bou] have measured enthalpy increments on three PbO_2-I samples of different origins between 365 and 657 K. Two sets of data differ by only about 2%, while the values of the third are 20% higher. The values of the two lower sets of data are in close agreement with the extrapolation of [85Cha] based on the low-temperature data of [68Dui]. The enthalpy of formation at 298 K was determined by [70Esp] as –274.5 ± 3 kJ/mol.

Table 9 Some Reactions of the Pb-O System in Air

Reaction	Temperature, K	Reference
PbO_2-I = $Pb_{12}O_{19}$ + O_2	553(a)	[1888Car]
	563(a)	[12Hem]
	553(a)	[29Mol]
	567 to 587(a)	[34Kru]
	553	[56But]
	535	[66Ott]
	545	[76Aba]
	502	This work
$Pb_{12}O_{19}$ = $Pb_{12}O_{17}$ + O_2	623	[45Bys]
	597	[56But]
	619	[66Ott]
	553	This work
$Pb_{12}O_{17}$ = Pb_3O_4-T + O_2.....	647	[56But]
	619	[66Ott]
	638	[76Aba]
	610	This work
Pb_3O_4-T = PbO-M + O_2.....	820	[1897Lec]
	810	[14Rei]
	810	[66Ott]
	835	[76Aba]
	803	[81Kha]
	808 ± 2 (exp.)	This work
	807 (opt.)	This work

(a) Decomposition temperature of PbO_2-I to lower oxides.

The data on the stability limits of the compounds $Pb_{12}O_{17}$, $Pb_{12}O_{19}$, and PbO_2-I are shown in Table 9 for air and in Fig. 17 for the other oxygen partial pressures. The three phase Pb_3O_4-T, $Pb_{12}O_{17}$, and $Pb_{12}O_{19}$ have been predicted to be in equilibrium at about 653 K and 2 bar O_2 based on the XRD analysis of annealed samples [64Whi, 65Roy]. The compound $Pb_{12}O_{17}$ is not stable at higher temperatures and pressures. This result is in agreement with the decomposition sequence PbO_2-I → $Pb_{12}O_{19}$ → Pb_3O_4-T observed at the higher pressures [37Hol, 40Hol, 64Whi, 65Roy] and the decomposition sequence PbO_2-I → $Pb_{12}O_{19}$ → $Pb_{12}O_{17}$ → Pb_3O_4-T observed at the lower ones [45Bys, 56But, 59And, 66Ott].

The phase boundary between PbO_2-I and $Pb_{12}O_{19}$ is uncertain because all the reported data were apparently based on decomposition experiments and the oxidation beyond the phase $Pb_{12}O_{19}$ has never succeeded. The only exception might have been in the study of [14Rei], who could measure release as well as absorption of oxygen at the decomposition point of

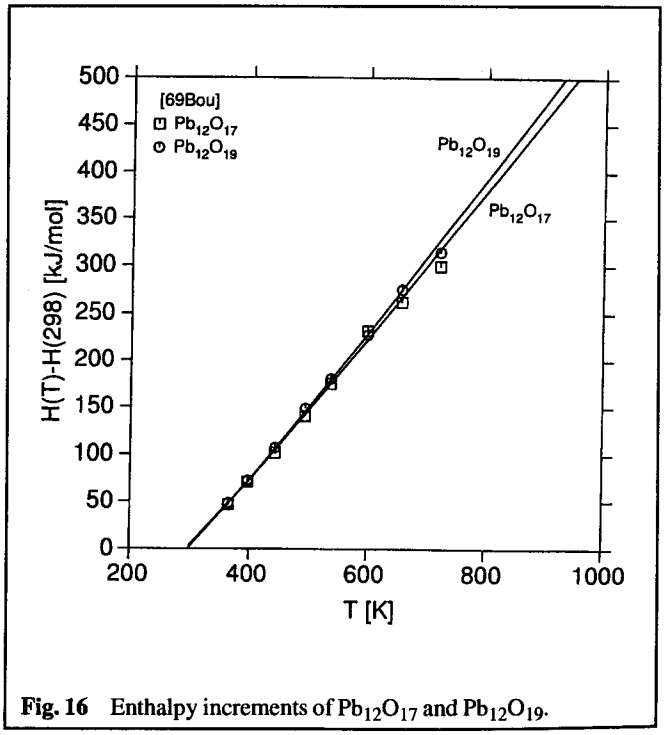

Fig. 16 Enthalpy increments of $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$.

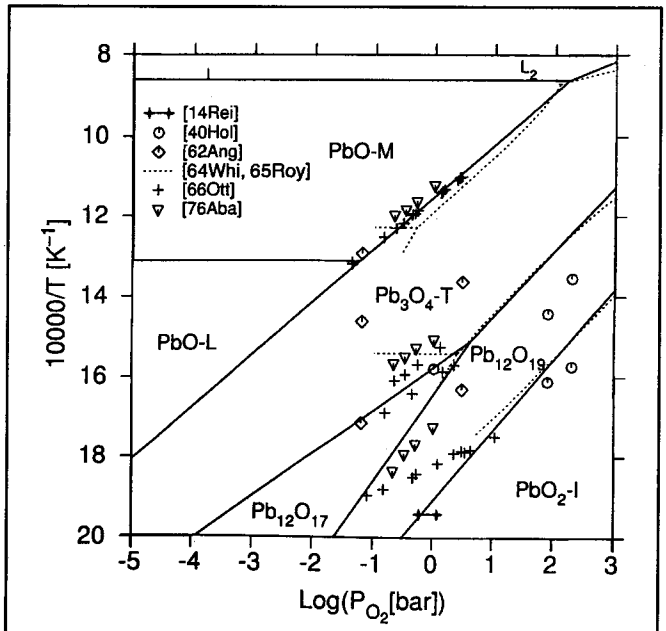

Fig. 17 Oxygen potential diagram at the higher oxygen pressures. The calculated fields of stability of the lead oxides are compared with the experimental data obtained at various oxygen pressures. The experimental data in air are listed in Table 9.

PbO_2-I. This evolution of oxygen was so slow that a precise value for the equilibrium oxygen pressure could not be obtained; however, it gives a limiting interval of 0.59 to 1.19 bar O_2 at 515 K. This observation places the decomposition temperature of PbO_2-I at a lower value than those reported from thermal analysis studies [1888Car, 12Hem, 29Mol, 34Kru, 56But, 76Aba] or other decomposition pressure measurements [66Ott] at the lower pressures. It is, however, fairly compatible with the extrapolation from the data at higher pressure [40Hol, 64Whi, 65Roy]. The equilibrium state should be approached faster in these latter studies because the temperature of the decomposition increases with the pressure. The slope of the higher pressure data is also in agreement with the one given by [76Aba]. The authors thus consider the values of [14Rei, 40Hol, 64Whi, 65Roy] to be the closest to the equilibrium state.

The stability limit between Pb_3O_4-T and $Pb_{12}O_{19}$ has been investigated by [37Hol], [40Hol], [64Whi], and [65Roy]. The difference between the values of [37Hol] and [40Hol] versus [64Whi] and [65Roy] is much larger than in the case of the PbO_2-I + $Pb_{12}O_{19}$ equilibrium. A precise determination of the transformation point seems difficult due to the unreactive behavior of Pb_3O_4-T toward oxidation [64Whi, 65Roy]. The results of [64Whi] and [65Roy] are more compatible with the other data on the $Pb_{12}O_{17}$ + Pb_3O_4-T equilibrium [66Ott, 76Aba] and are thus preferred here.

Data on the equilibria $Pb_{12}O_{19}$ + $Pb_{12}O_{17}$ and $Pb_{12}O_{17}$ + Pb_3O_4-T are scarce and uncertain. The reported values were obtained from the study of the decomposition of PbO_2-I. $Pb_{12}O_{19}$ and $Pb_{12}O_{17}$ have also been obtained from the oxidation of PbO samples, but the transformation points are difficult to determine, again because of the unreactive behaviour of Pb_3O_4-T and the formation of the metastable solid solutions. The lowest values for the decomposition temperature of $Pb_{12}O_{19}$ and $Pb_{12}O_{17}$ have been given by [66Ott]. However, even in his study, the reversibility of the reaction could only be observed for the Pb_3O_4-T + PbO-M equilibrium. The slope of his data on the $Pb_{12}O_{17}$ + Pb_3O_4-T equilibrium is in good agreement with the one reported by [76Aba] and, at least, these measured dissociation pressures may be close to equilibrium. Their other data on the $Pb_{12}O_{19}$ + $Pb_{12}O_{17}$ and PbO_2-I + $Pb_{12}O_{19}$ equilibria are less reliable. The PbO_2-I + $Pb_{12}O_{19}$ equilibrium is discussed above. In the case of the equilibria $Pb_{12}O_{19}$ + $Pb_{12}O_{17}$, the values given by [66Ott] together with the slope from his data on $Pb_{12}O_{17}$ + Pb_3O_4-T would lead to an increase in the stability of $Pb_{12}O_{17}$ with an increase in temperature and pressure, which is not compatible with the observations at higher pressures [40Hol, 64Whi, 65Roy].

2.4 The Gas Phase

The vaporization of lead oxides has been studied using mass spectrometry by [65Dro], [68Kaz], and [69Chi]. Samples of PbO_2 were found to decompose upon heating into O_2 and lower oxides, and all samples vaporized further in the same way as PbO-M [65Dro]. Pb, PbO, Pb_2O_2, Pb_3O_3, Pb_4O_4, and O_2 were reported as the major gas species in both studies [65Dro, 68Kaz, 69Chi]. The species Pb_5O_5, and Pb_6O_6 were also detected at the highest temperature of measurement (1200 K) [65Dro].

Previous to these studies, the total pressure over PbO-M had been measured by numerous authors using Knudsen, Langmuir, and transport methods and assuming the vapor to contain only the molecule PbO. The partial pressure of PbO was then recalculated from all these studies by [65Dro] by taking the presence of the other species into account. Their analysis of previous data led to the average value of 288.3 kJ/mol for the enthalpy of sublimation of PbO-M to the gas monomer PbO, compared to 289.5 kJ/mol obtained from their mass-spectrometric data. The boiling point of PbO has been determined by [64Kna] as 1808 K. Earlier measurements are discussed in [64Kna].

3. Thermodynamic Models

The present thermodynamic description is aimed for calculations at temperatures above 298 K and at a total pressure of 1 bar. Extrapolations at higher oxygen partial pressures are shown up to 100 bar O_2 where the effect of the total pressure on the condensed phases is assumed to remain small. The phases Pb_3O_4-R, Pb_2O_3, PbO_2-II, and PbO_2-III, whose range of stability presumably lies outside these limits, are therefore not considered in this work.

The pure elements in their stable states at 298 K were chosen as the reference state of the system. The thermodynamic properties of the pure elements are not discussed here, and the Gibbs energy functions were taken from [91Din].

3.1 Solid Phases

All solid phases are approximated here as stoichiometric compounds. Gibbs energy functions were determined for the phases PbO-L, PbO-M, Pb_3O_4-T, $Pb_{12}O_{17}$, $Pb_{12}O_{19}$, and PbO_2-I, which are considered as equilibrium phases of the system. The Gibbs energy function for fcc Pb was taken from [91Din].

3.2 Liquid Phase

A large miscibility gap separates the metal liquid (L_1) from the oxide one (L_2). Nevertheless, the liquid phase is described here in the whole composition range by a single model, the two-sublattice ionic liquid model [85Hil], for compatibility with other assessments of metal-oxygen systems and because the miscibility gap will eventually close at high temperature.

The composition of L_2 is expected to extend slightly beyond 50 at.% O at high oxygen partial pressures where, as mentioned above, a eutectic decomposition into PbO-M and Pb_3O_4-T was observed. This could be taken into account in the model description, but was neglected here because there are no reliable data on the composition of oxygen-saturated L_2 and because any excess of oxygen in regard to the PbO composition will probably remain extremely small, at least at ambient pressures. This simplification is also convenient for later calculations in multicomponent systems. Furthermore, a model description of this possible small excess of oxygen in L_2 should be considered together with the oxygen nonstoichiometry in the solid PbO phases. Therefore, the authors have applied the formula $(Pb^{2+})_2(Va^{2-},O^{2-})_2$, which

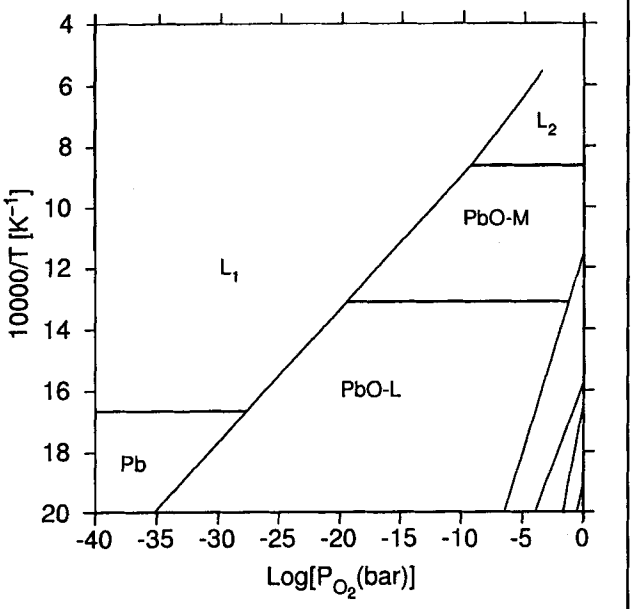

Fig. 18 Oxygen potential diagram at the lower oxygen pressures.

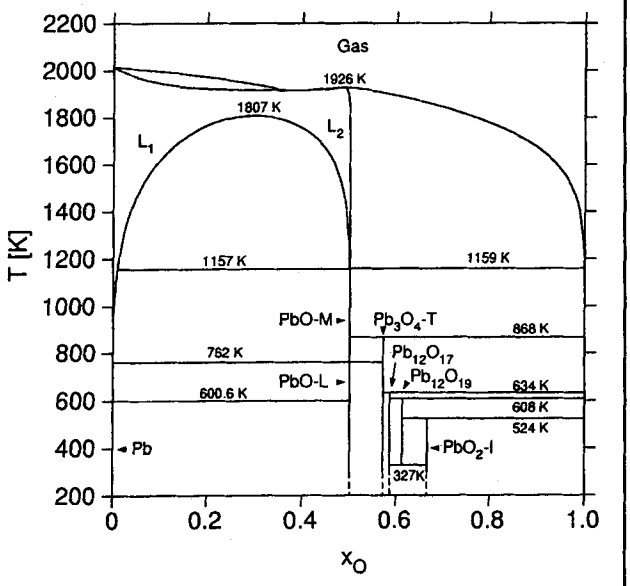

Fig. 19 Phase diagram of the Pb-O system at 1 bar.

restricts the range of existence of the liquid phase to the Pb-PbO interval. The two-sublattice formalism leads then to the following expression for the molar Gibbs energy of the liquid phase:

$$G^{0,L} = 2y_{Va^{2-}} G^{0,L}_{Pb} + 2y_{O^{2-}} G^{0,L}_{PbO} + 2RT\left(y_{Va^{q-}} \ln\left(y_{Va^{q-}}\right) + y_{O^{2-}} \ln\left(y_{O^{2-}}\right)\right) + G^{ex,L}$$

where $G^{0,L}_{Pb}$, standing for $G^{0,L}_{Pb^{2+}:Va^{2-}}$, represents the Gibbs energy of 1 mole of pure Pb liquid, and $G^{0,L}_{PbO}$, standing for $\frac{1}{2}\, G^{0,L}_{Pb^{2+}:O^{2-}}$, represents the Gibbs energy of 1 mole of ideal PbO liquid. y_i is the site fraction, that is, the fraction of i on the sublattice, and $G^{ex,L}$ is the excess Gibbs energy, described in this work by the formula:

$$G^{ex,L} = y_{Va^{2-}} y_{O^{2-}} \left(L^{0,L} + \left(y_{Va^{2-}} - y_{O^{2-}}\right) L^{1,L}\right)$$

where $L^{0,L}$, standing for $L^{0,L}_{Pb^{2+},Va^{2-}:O^{2-}}$ and $L^{1,L}$, standing for $L^{1,L}_{Pb^{2+},Va^{2-}:O^{2-}}$, are interaction parameters to be determined together with $G^{0,L}_{PbO}$. The function for $G^{0,L}_{Pb}$ was taken from [91Din]. Two excess parameters $L^{0,L}$ and $L^{1,L}$ are considered here, and both are taken as linear function of the temperature because there are solubility and activity data at several concentrations and temperatures for both L_1 and L_2. This allows modeling of an asymmetric miscibility gap and description of different temperature dependencies for the solubility limits for L_1 and L_2.

3.3 Gas Phase

The gas phase is treated as an ideal mixture containing the species Pb, Pb_2, PbO, Pb_2O_2, Pb_3O_3, Pb_4O_4, Pb_5O_5, Pb_6O_6, O, O_2, and O_3. The Gibbs energy for 1 mole of formula units is given as:

$$G^{0,G} = \sum_i {}^{I}y_i \left(G_i^{0,G} + RT \ln\left(y_i\right)\right) + RT \ln\left(P\right)$$

where y_i is the mole fraction of species i in the gas phase, and $G_i^{0,G}$ its molar Gibbs energy. The total pressure is given by P.

A thermodynamic description of the Pb-O gas phase including all known species has recently been given by [87Lam] and is based on the data of [65Dro]. The type of polynomials they used to represent the Gibbs energy do not correspond to the integration of an equation for the specific heat. Here the authors preferred to use the functions given in the SGTE thermochemical database [94SGT] for the species Pb, Pb_2, PbO, O, O_2 and O_3. The function for PbO was then readjusted to be consistent with their thermodynamic description of the condensed phases, and the functions for the species Pb_2O_2, Pb_3O_3, Pb_4O_4, Pb_5O_5, and Pb_6O_6 were fitted to the experimental data.

4. Optimization of Parameters and Discussion

The optimization of the thermodynamic parameters and all calculations were performed using the Thermo-Calc software [85Sun]. The resulting parameters are presented in Table 10. The calculated fields of stability of the lead oxides as a function of the temperature and the oxygen partial pressure are shown in Fig. 17 and 18. The calculated phase diagram of the Pb-O system at 1 bar is shown in Fig. 19.

The thermodynamic properties of PbO-M are the best known part of the Pb-O system. $G^{0,PbO-M}$ was thus determined first and then kept constant. The heat capacity of PbO-M was

Table 10 Optimized Thermodynamic Description of the Pb-O System

PbO-L

$G^{0,PbO-L} = -235\,043 + 250.4T - 46.2\,T\ln(T) - 0.008\,T^2 + 225\,000\,T^{-1}$

PbO-M

$G^{0,PbO-M} = -232\,910 + 244.7\,T - 45.9\,T\ln(T) - 0.0067\,T^2 + 178\,000\,T^{-1}$

Pb_3O_4-T

$G^{0,Pb_3O_4-T} = -802\,140 + 1112\,T - 194.5\,T\ln(T) + 0.0025\,T^2 + 1\,566\,000\,T^{-1}$

$Pb_{12}O_{17}$

$G^{0,Pb_{12}O_{17}} = 3.5\,G^{0,Pb_3O_4-T} + 1.5\,G^{0,PbO_2-1} - 33\,000 + 40\,T$

$Pb_{12}O_{19}$

$G^{0,Pb_{12}O_{19}} = 2.5\,G^{0,Pb_3O_4-T} + 4.5G^{0,PbO_2-1} - 9000 - 16\,T$

PbO_2-I

$G^{0,PbO_2-1} = -305\,000 + 385.6\,T - 67\,T\ln(T) - 0.007\,T^2 + 400\,000\,T^{-1}$

Liquid

$G^{0,L}_{PbO} = -219\,210 + 360\,T - 65\,T\ln(T)$

$L^{0,L}_{Pb^{2+}+Va,O^{2-}} = +168\,750 - 61\,T$

$L^{1,L}_{Pb^{2+}:Va,O^{2-}} = +29\,510 - 20\,T$

Gas

$G^{0,G}_{PbO} = G^{0,G}_{PbO}(SGTE) - 2710$

$G^{0,G}_{Pb_2O_2} = 2\,G^{0,G}_{PbO} - 268\,600 + 148\,T$

$G^{0,G}_{Pb_3O_3} = 3\,G^{0,G}_{PbO} - 527\,400 + 296\,T$

$G^{0,G}_{Pb_4O_4} = 4\,G^{0,G}_{PbO} - 818\,100 + 444\,T$

$G^{0,G}_{Pb_5O_5} = 5\,G^{0,G}_{PbO} - 1\,055\,000 + 592\,T$

$G^{0,G}_{Pb_6O_6} = 6\,G^{0,G}_{PbO} - 1\,343\,000 + 740\,T$

$G^{0,G}_{Pb} = +188\,835.507 - 32.9195926\,T - 21.30643\,T\ln(T) + 6.551465\times10^{-4}\,T^2 + 9337.21\,T^{-1} - 1.4308295\times10^{-7}\,T^3$ (298 < T <1100)

$= +186\,417.546 + 1.1925361\,T - 26.43463\,T\ln(T) + 0.004836378\,T^2 + 151\,170.2\,T^{-1} - 7.36003167\times10^{-7}\,T^3$ (1100 < T <2000)

$= +284\,618.057 - 556.413056\,T + 46.90369\,T\ln(T) + 0.01960158\,T^2 - 24\,599\,010\,T^{-1} + 7.96842\times10^{-7}\,T^3$ (2000 < T <3700)

$G^{0,G}_{Pb_2} = +294\,478.493 - 30.0067503\,T - 36.885\,T\ln(T) - 0.001044156\,T^2 - 834.586\,T^{-1} - 1.93234833\times10^{-8}\,T^3$ (298 < T <1400)

$= +308\,511.945 - 91.1346139\,T - 29.46399\,T\ln(T) - 0.001186672\,T^2 - 3\,780\,887\,T^{-1} - 2.884025\times10^{-7}\,T^3$ (1400 < T <2300)

$= +400\,773.9 - 645.007872\,T + 43.76939\,T\ln(T) - 0.02616466\,T^2 - 24\,494\,475\,T^{-1} + 1.27101733\times10^{-6}\,T^3$ (2300 < T <3500)

$G^{0,G}_{PbO}(SGTE) = +57\,091.4835 - 12.9608905T - 33.41877\,T\ln(T) - 0.0034174485\,T^2 + 119\,823.95\,T^{-1} + 4.87887167\times10^{-7}\,T^3$ (298 < T <1000)

$= +50\,999.6993 + 44.2651041\,T - 41.6039\,T\ln(T) + 0.001760351\,T^2 + 1\,005\,370\,T^{-1} - 1.68793667\times10^{-7}\,T^3$ (1400 < T <3000)

$G^{0,G}_{O} = +243\,206.494 - 20.8612587\,T - 21.01555\,T\ln(T) + 1.2687055\times10^{-4}\,T^2 - 42897.09\,T^{-1} - 1.23131283\times10^{-8}\,T^3$ (298 < T <2950)

Functions from other sources

$G^{0,Pb}$ and $G^{0,G}_{O_2}$ from [91Din]. $G^{0,G}_{Pb}$, $G^{0,G}_{Pb_2}$, $G^{0,G}_{PbO}$ (*SGTE*), $G^{0,G}_{O}$, and $G^{0,G}_{O_3}$ from [94SGT].

$G^{0,G}_{O_3} = +130\,696.944 - 37.9096651\,T - 27.58118\,T\ln(T) - 0.02763076T^2 + 99\,530.45\,T^{-1} + 4.60539333\times10^{-6}\,T^3$ (298 < T <700)

$= +114\,760.623 + 176.626736\,T - 60.10286\,T\ln(T) + 0.00206456\,T^2 + 1\,572\,175\,T^{-1} - 5.17486667\times10^{-7}\,T^3$ (700 < T <1300)

$= +49\,468.3958 + 710.094819\,T - 134.3696\,T\ln(T) + 0.039707355\,T^2 + 12\,362\,250\,T^{-1} - 4.10457667\times10^{-6}\,T^3$ (1300 < T <2100)

$= +866\,367.075 - 3566.80563\,T + 421.2001\,T\ln(T) - 0.1284109\,T^2 - 2.1304835\times10^{8}\,T^{-1} + 5.44768833\times10^{-6}\,T^3$ (2100 < T <2800)

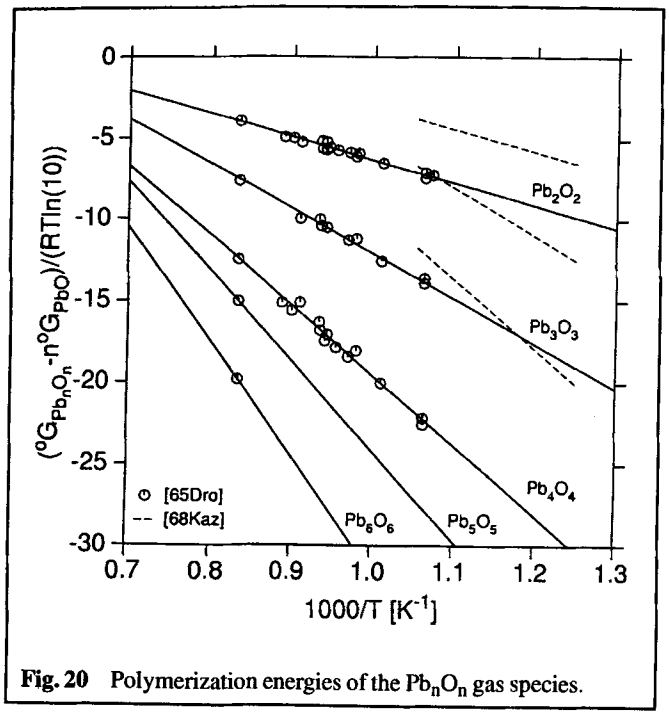

Fig. 20 Polymerization energies of the Pb_nO_n gas species.

fitted to the data of [58Kin], [60Kos], [42Spe], [61Rod], and [64Kna]. The calculated heat capacity and enthalpy increments are shown in Fig. 3 and Fig. 4, respectively. The remaining parameters of $G^{0,PbO-M}$ were determined from the entropy data of [60Kos], the values of the enthalpy and Gibbs energy of formation at 298 K [70Esp, 32Spe], and mostly high-temperature emf data [64Alc, 64Mat1, 64Mat2, 68Cha, 71Jac, 72Szw, 75Cal, 76Cha, 79Tas, 80Sug, 84Ban, 95Mal]. The emf results were treated statistically and given a large weight. The resulting difference between the calculated Gibbs energy of formation at higher temperatures and the experimental data is presented in Fig. 5. The calculated values for the enthalpy and Gibbs energy of formation at 298 K are then less negative by about 0.6 kJ/mol than the reported values [70Esp, 32Spe] that are listed in Table 1. This discrepancy lies in the uncertainty range given by [85Cha] and can be accepted.

The heat capacity of PbO-L was fitted to the data of [58Kin] and the enthalpy increments of [42Spe]. The results are shown in Fig. 1 and 2, respectively. The remaining parameters of $G^{0,PbO-L}$ were adjusted to the entropy value selected by [85Cha], the enthalpy difference between PbO-L and PbO-M measured by [64Kna], the Gibbs energy of formation data at 298 K [23Smi, 32Spe], and the selected value of the transformation temperature [34Coh, 41Pet, 46Kam, 46Pam, 68Cou]. The thermodynamic properties at 298 K are listed in Table 1. The data on the transformation between PbO-L and PbO-M are presented in Table 2 and Table 3. The agreement among the experimental data and with the calculated values of the thermodynamic properties is good. The uncertainty in the temperature of the PbO-L ↔ PbO-M transformation is discussed above.

The parameters of the liquid phase were fitted to as few data as possible, but to those that could be considered as the most reliable. Values subject to controversy, such as the oxygen solubility limit in L_1 in the higher or lower temperature ranges, were not used, but the compatibility between various sets of data throughout the entire composition range was tested at a preliminary stage. The parameters of the liquid phase were optimized simultaneously except for the heat capacity of liquid PbO, which was kept fixed at the value 65 J/mol · K based on the data of [61Rod] and [64Kna]. The other parameters of $G^{0,L}_{PbO}$ were constrained by the selected emf data discussed above [64Mat1, 64Mat2, 68Cha, 71Jac, 72Szw, 75Cal, 76Cha, 76Leu, 77Sug, 79Tas], and the data on the temperature [34Gel, 36Kra] and enthalpy [61Rod, 64Kna, 71War] of melting. The parameters $L^{0,L}$ and $L^{1,L}$ were constrained by the following data on L_1 and L_2: selected values of the oxygen solubility in L_1 at intermediate temperatures [59Bra, 64Alc, 74Kux, 79Tas], data on the oxygen activity in L_1 below 1 at.% O [76Cha, 77Ise, 79Ots, 79Tas, 81Ots], assessed monotectic temperature [88Wri], solubility limit of Pb-saturated L_2 up to 1273 K [74Kux, 77Ise], and activity data in L_2 [77Ise].

The calculated values at the melting point of PbO-M are shown in Tables 5 and 6. The thermodynamic properties of liquid PbO are presented in Fig. 4 and 6. These values seem well established. The calculated solubility limit of oxygen in L_1 is compared with the experimental data in Fig. 7. The shape of the miscibility gap cannot be changed significantly without creating a major deviation from the data on the oxygen activity in L_1. A closer fit to the lower (for example, [74Kux]) or the higher (for example, [77Ise]) values of the oxygen saturation would be in contradiction with the data of [79Ots, 79Tas, 81Ots]. The oxygen activity in L_1 and the derived Gibbs energy of dissolution of gaseous oxygen in liquid Pb at infinite dilution are plotted in Fig. 8 and 9, respectively. These figures emphasize the good agreement with all the activity data at oxygen concentration below 1 at.% and the importance attributed to the values of [79Ots], [79Tas], and [81Ots] in the present optimization.

The calculated values for the eutectic and monotectic reactions are shown in Table 8. The calculated eutectic composition of L_1 is in good agreement with the extrapolation of [55Ric] and the assessment of [79Tas] and [88Wri]. The calculated composition of L_1 at the monotectic reaction agrees with the analysis of [88Wri], but the monotectic temperature is predicted to be very close to the melting temperature of PbO-M (used by [55Ric], [64Alc], and [72Szw]) in contradiction to the recent studies of [74Kux], [76Cha], [77Ise], and [79Tas]. This is discussed below in relation with the data on L_2.

The calculated solubility limits of L_2 are shown in Fig. 10. The data of [74Kux], and [77Ise] are in close agreement below 1273 K and are well reproduced by the optimized curve. At higher temperatures, the calculated solubility limit tends to be closer to the data of [77Ise], which is due to the fact that the activity values from that study were used in the optimization. The calculated activity of oxygen in L_2 is then compared with these experimental data in Fig. 11. The present calculation represents the closest fit to these data that could be obtained without influencing the miscibility gap so much that conflicts would arise with the adopted data on the metallic side. It may be also expected that a closer fit would be obtained when considering the possibility of oxygen excess in L_2. However, the authors could not create significant changes by expanding our model description beyond the PbO composition. Looking back at the monotectic reaction, it is evident from Fig. 10 that the tempera-

ture of this equilibrium is mainly determined by the very flat slope of the L_2 + PbO-M liquidus. This is very closely related to the enthalpy of melting of PbO-M, which is well established. It was therefore almost impossible to impose any variation in the calculated value of the monotectic temperature. Nevertheless, the experimental evidences for a value around 1143 K are strong, and the present discrepancy may be due to the influence of the oxygen nonstoichiometry in PbO-M, which was neglected here.

The parameters of $G^{0,Pb_3O_4\text{-}T}$ were fitted to the data on the heat capacity [29Mil], the enthalpy increments [69Bou], the entropy at 298 K [85Cha], and the transformation between PbO-M and Pb_3O_4-T [14Rei, 64Whi, 66Ott, 81Kha, this work]. The calculated results are shown in Table 1 and Fig. 12 to 14, respectively. The calculated line in Fig. 14 has a slightly more pronounced curvature than the experimental data suggest. This curvature was much stronger in preliminary calculations, which gave a drastic decrease in the stability of PbO-M in favor of Pb_3O_4-T at higher temperatures and pressures. This effect could be partially reduced by small variations in the heat capacity of these phases, that is, by a small increase in the heat capacity of PbO-M or a small decrease in the one of Pb_3O_4-T. This is also an argument to give more weight to the data of [64Kna] for PbO-M. The present optimized values for PbO-M differ only slightly from the fit of [85Cha] to the data of [61Rod], as can be seen from Fig. 4. The difference between the assessment of [85Cha] and this optimization is more marked in the case of the enthalpy increments of Pb_3O_4-T shown in Fig. 13. The data on the stability limit between PbO-M and Pb_3O_4-T was discussed above. The calculated conditions of the equilibrium between L_2, PbO-M, and Pb_3O_4-T are in close agreement with the studies of [64Whi] and [65Roy].

The heat capacity of PbO_2-I was based on the assessment of [85Cha]. The calculated results agree well with the data of [23Pal], [68Dui], and [69Bou], as can be seen from Fig. 12 and 13. No parameter was used to describe the heat capacity of $Pb_{12}O_{17}$ and $Pb_{12}O_{19}$, and the calculated values are given by those of Pb_3O_4-T and PbO_2-I following the rule of Neumann-Kopp. This simplification leads to enthalpy increments in close agreement with the measured data, as can be seen from Fig. 16. The other parameters of $G^{0,PbO_2\text{-}I}$ and $G^{0,Pb_{12}O_{19}}$ were adjusted simultaneously to the data on the thermodynamic properties at 298 K [70Esp, 29Mil, 63Cha, 68Dui] and the selected data on the phase stability limits [14Rei, 64Whi, 65Roy]. The function $G^{0,Pb_{12}O_{17}}$ was obtained by fitting the entropy of formation of $Pb_{12}O_{17}$ to the slope observed by [66Ott, 76Aba] for the equilibrium $Pb_{12}O_{17}$ + Pb_3O_4-T, and subsequently adjusting the enthalpy of formation of $Pb_{12}O_{17}$ to reproduce the conditions of the three-phase equilibrium $Pb_{12}O_{19}$ + $Pb_{12}O_{17}$ + Pb_3O_4-T reported by [64Whi]. These parameters were strongly rounded to account for the uncertainty in their values.

The data on the stability limits of the higher oxides $Pb_{12}O_{17}$, $Pb_{12}O_{19}$, and PbO_2-I were discussed above. The calculated fields of stability are shown in Fig. 17. The thermodynamic properties at 298 K are given in Table 1. The agreement between these results is convincing in view of the large uncertainties in the data on the PbO-PbO_2 part of the system.

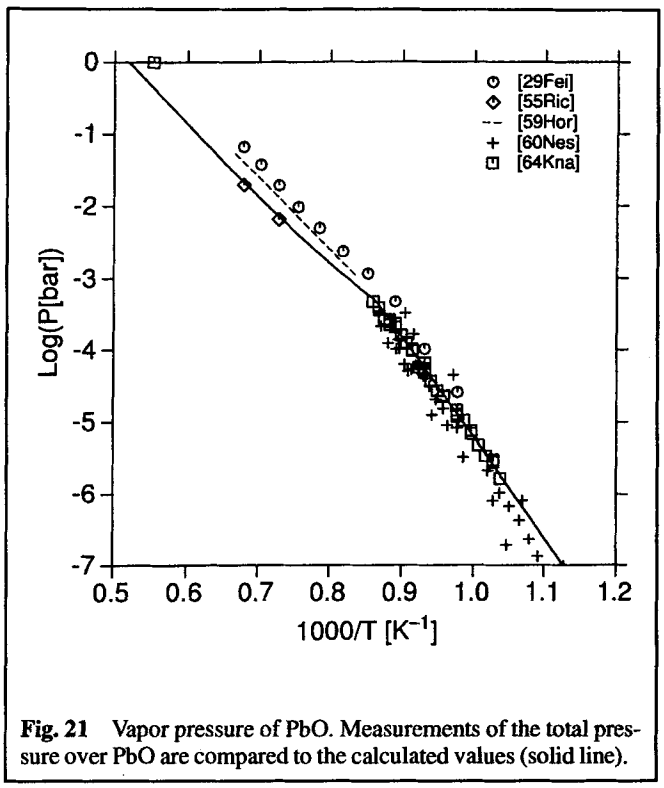

Fig. 21 Vapor pressure of PbO. Measurements of the total pressure over PbO are compared to the calculated values (solid line).

The functions $G^{0,G}_{Pb_2O_2}$, $G^{0,G}_{Pb_3O_3}$, $G^{0,G}_{Pb_4O_4}$, $G^{0,G}_{Pb_5O_5}$ and $G^{0,G}_{Pb_6O_6}$ for the gas species were based on $G^{0,G}_{PbO}$ and parameters for the enthalpy and entropy of polymerization were fitted to the data of [65Dro]. The data for Pb_nO_n (n = 2, 3, 4) could be well reproduced, within the uncertainty of the fit, by adopting the value 148n J/mol · K for the entropies of polymerization. Thus, this relationship was also adopted for the other two species, Pb_5O_5, and Pb_6O_6, for which data were available at 1200 K only. The results are shown in Fig. 20. To ensure the thermodynamic consistency between the condensed phases and the gas phase, the value –2710 J/mol was added to the function $G^{0,G}_{PbO}$ (SGTE) taken from the SGTE data base [94SGT]. This correction leads to good agreement with the reported data on the vapor pressure over PbO as shown in Fig. 21. Partial pressures calculated with this description are in close agreement with the one shown by [87Lam].

5. Conclusions

The lead-oxygen system has been the subject of numerous studies that have unfortunately produced many contradictory results. Some parts of the system had been previously assessed independently without consideration for the entire composition range. The present thermodynamic optimization clarifies the compatibility between various sets of data, in particular concerning the liquid phase and the higher oxides of lead. The model description of the liquid phase leads to solubility and activity data of the Pb-rich liquid in good agreement with the most recent assessments and to solubility limits and thermodynamic properties of the PbO-rich liquid

reproducing well the experimental results. The calculated miscibility gap is predicted to close just above 1800 K. The analysis of the PbO-PbO_2 part of the system shows that a thermodynamic description in close agreement with the most reliable data on the stability limits of the higher oxides as well as their thermodynamic properties at 298 K can be found. The resulting description offers a consistent set of Gibbs energy functions for the Pb-O system and allows the further modeling of multicomponent lead oxide systems. Finally, the oxygen nonstoichiometry of the PbO phases was not considered here and appears as an important subject of analysis for future improvements of the thermodynamic description of the Pb-O system.

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