O – Pb (Oxygen – Lead)

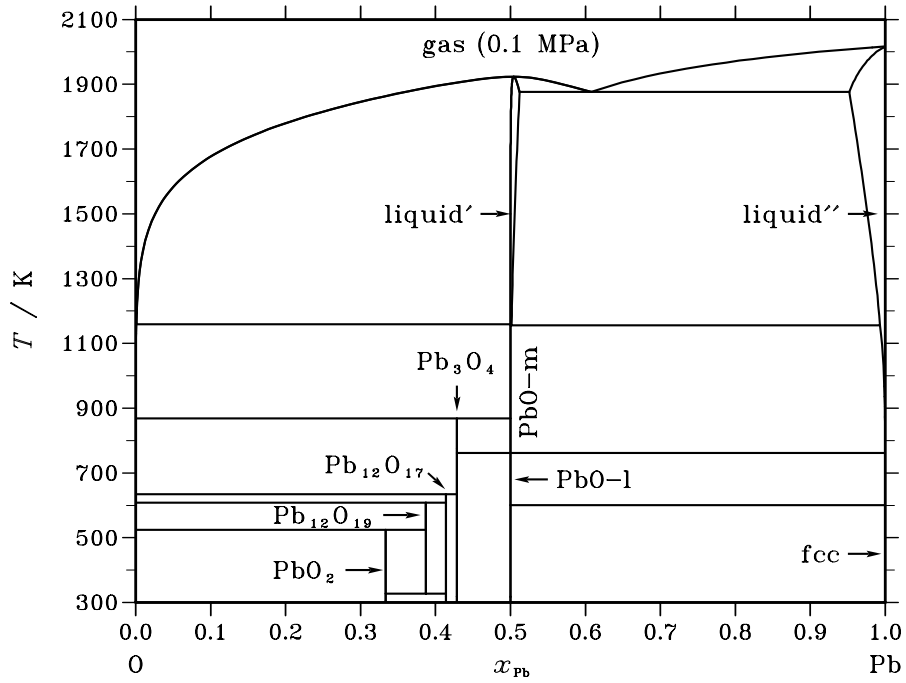

Fig. 1. Calculated phase diagram for the system O-Pb.

The O-Pb system is of primary technical importance because of the wide use of lead-bronze, lead-tin solders, and lead-acid accumulators. Lead oxides are also components of piezoelectric and high-temperature superconducting ceramics. The O-Pb system was reviewed by [88Wri], who gave an exhaustive summary of the numerous studies and discussed the controversies and uncertainties.

A consistent thermodynamic description of the O-Pb system through the entire composition range has been published by [98Ris]. The gas phase was 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 liquid phase was described by a two-sublattice partially ionic liquid model which allows compositional variations between Pb and PbO. The solid phases PbO-l, PbO-m, Pb_3O_4, $Pb_{12}O_{17}$, $Pb_{12}O_{19}$, and PbO_2 were approximated as stoichiometric compounds and the fcc phase was considered as pure lead. The thermodynamic description is in close agreement with the most reliable data on the stability limits of the higher oxides in the PbO-PbO_2 part. For the Pb-PbO range, the spread in the data concerning the miscibility gap in the liquid phase is large and results of the least-squares optimisation depend on the selected dataset. All experimental studies are confined to temperatures below 1473 K. The choice made in [98Ris] results in the calculated phase diagram at 1 bar pressure, where the miscibility gap is predicted to close just above 1800 K.

Recently, the description of the liquid phase in O-Pb has been modified in conjunction with the thermodynamic optimisation of the ternary Cu-O-Pb system [03Zin]. The experimental data of the ternary system indicate a lower solubility limit of oxygen in the Pb-rich liquid than calculated with the description of [98Ris] and thus, another dataset has been preferred. The critical point of the miscibility gap is then shifted to about 4700 K. The new set of thermodynamic parameters obtained in [03Zin] is recommended, since it is based on reasonable data selection by applying additional constraints from a ternary system.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_LIQUID	$Pb_p^{2+}(O^{2-},\square)_q$
PbO_2	$C4$	TiO_2(rutile)	$tP6$	$P4_2/mnm$	PBO2	Pb_1O_2
$Pb_{12}O_{19}$	⋯	⋯	$mP62$	Pc or $P2_1/c$	PB12O19	$Pb_5^{2+}Pb_7^{4+}O_{19}^{2-}$
$Pb_{12}O_{17}$	⋯	⋯	$oP58$?	$Pmc2_1$?	PB12O17	$Pb_7^{2+}Pb_5^{4+}O_{17}^{2-}$
Pb_3O_4	⋯	Pb_3O_4-t	$tP28$	$P4_2/mbc$	PB3O4	Pb_3O_4
PbO-m	⋯	PbO-m	$oP8$	$Pbma$	PBO_M	Pb_1O_1
PbO-l	$B10$	PbO-l	$tP4$	$P4/nmm$	PBO_L	Pb_1O_1
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	Pb_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Pb}			$\Delta_r H$ / (J/mol)
gas ⇌ liquid′	congruent	1923.6	0.504	0.504		−85481
gas ⇌ liquid′ + liquid″	gas-eutectic	1876.7	0.608	0.512	0.952	−97273
gas + liquid′ ⇌ PbO-m	gas-peritectic	1158.6	0.001	0.500	0.500	−13399
liquid′ ⇌ PbO-m + liquid″	monotectic	1156.0	0.501	0.500	0.993	−13560
gas + PbO-m ⇌ Pb_3O_4	gas-peritectoid	868.7	0.000	0.500	0.429	−10580
PbO-m ⇌ PbO-l	polymorphic	761.8	0.500	0.500		−513
gas + Pb_3O_4 ⇌ $Pb_{12}O_{17}$	gas-peritectoid	634.2	0.000	0.429	0.414	−3083
gas + $Pb_{12}O_{17}$ ⇌ $Pb_{12}O_{19}$	gas-peritectoid	608.5	0.000	0.414	0.387	−2864
liquid″ ⇌ PbO-l + fcc	degenerate	600.6	1.000	0.500	1.000	−4774
gas + $Pb_{12}O_{19}$ ⇌ PbO_2	gas-peritectoid	524.1	0.000	0.387	0.333	−7570
$Pb_{12}O_{19}$ ⇌ PbO_2 + $Pb_{12}O_{17}$	eutectoid	326.9	0.387	0.333	0.414	−470

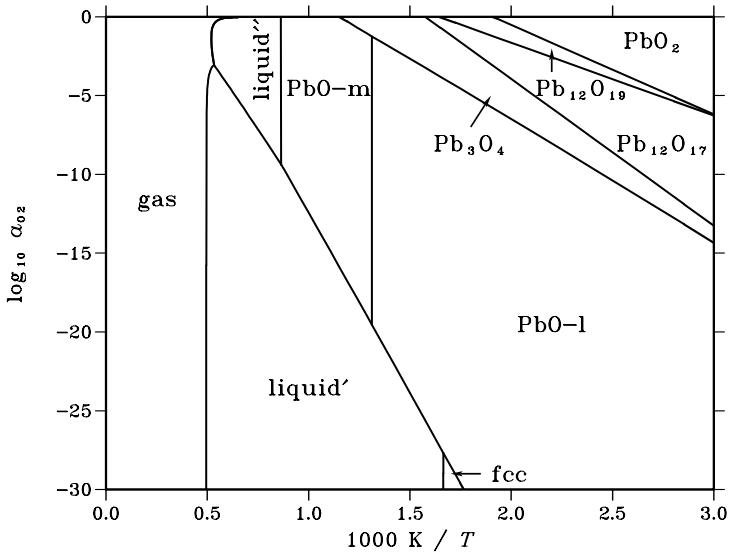

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}O_2$(gas, 0.1 MPa).

Table III. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Pb}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
PbO_2	0.333	−74226	−93906	−66.009	1.988
$Pb_{12}O_{19}$	0.387	−82425	−100332	−60.060	2.600
$Pb_{12}O_{17}$	0.414	−86559	−104226	−59.257	2.904
Pb_3O_4	0.429	−87964	−104775	−56.384	3.072
PbO-l	0.500	−94469	−109524	−50.495	2.193
PbO-m	0.500	−94019	−108718	−49.301	2.184

References

[88Wri] H.A. Wriedt: Bull. Alloy Phase Diagrams **9** (1988) 106–127.
[98Ris] D. Risold, J.-I. Nagata, R.O. Suzuki: J. Phase Equilibria **19** (1998) 213–233.
[03Zin] M. Zinkevich, M. Cancarevic, F. Aldinger: unpublished optimization, 2003.