The ideal-gas thermochemistry of PbO can be deduced by combining its dissociation energy with literature thermochemistry for gaseous Pb and O atoms. The enthalpy of formation of PbO is given by

The subscript “0” indicates that values are for the temperature *T* = 0. Reference values of are (195.8 ± 0.8) kJ/mol for Pb {Gurvich, 1989 #157} and (246.844 ± 0.002) kJ/mol for O {Ruscic, 2024 #11101}. Combined with *D*0 = (376 ± 3) kJ/mol [this is only a placeholder value], this gives = (67 ± 3) kJ/mol. This value is consistent with the experimental value of (70.4 ± 4.0) kJ/mol recommended by Gurvich et al. {Gurvich, 1989 #157}. However, our value is substantially lower than that calculated by Minenkov et al. in their study of dozens of challenging molecules {Minenkov, 2017 #4203}.

Minenkov et al. {Minenkov, 2017 #4203} avoided atomization reactions for deriving thermochemistry. This was done for technical reasons, but also has the theoretical benefit of conserving the number of electron pairs {Snyder, 1969 #2652;Hehre, 1970 #218}. For PbO, they selected the reaction

which has the added benefit of using two elements in their standard states (for which by definition). The experimental value = (-238.90 ± 0.02) kJ/mol is well established {Ruscic, 2024 #11101}. Among the experimental alternatives for PbCl2, Minenkov et al. selected = (-174.1 ± 1.3) kJ/mol {Chase, 1998 #850}. The corresponding value at zero temperature is = (-172.0 ± 1.3) kJ/mol {Chase, 1998 #850}.

Table A shows CCSD(T) energies for reaction (2), not including vibrational zero-point energy (ZPE) or spin-orbit stabilization energy (*E*so). The estimated uncertainties are simply the distances of the energy extrapolations.

**Table A.**  CCSD(T) reaction energies (kJ/mol) for reaction (2), without ZPE or *E*so, computed using two basis sets and with two procedures for basis-set extrapolation. Geometries are from CCSD(T)/actzpp.

|  |  |
| --- | --- |
| Basis set | D*E* |
| acqzpp | 519.7 |
| ac5zpp | 521.3 |
| CBS-A | 523.5 ± 2.3 |
| CBS-B | 523.1 ± 1.8 |

Experimental values of ZPE are (279.22 ± 0.04) and (2179.3 ± 0.2) cm-1 for Cl2 and H2, respectively {Irikura, 2007 #2079}, and (4636 ± 20) cm-1 for H2O {Irikura, 2009 #2204}. Analyzing experimental spectroscopic data {Enomoto, 2024 #11070} using the method of ref. {Irikura, 2007 #2079} leads to an experimental value ZPE(PbO) = (359.6 ± 0.6) cm-1. (Uncertainties are 2σ, i.e. with coverage factor *k* = 2.) For PbCl2, experimental spectroscopic data are limited to approximate values of the fundamental frequencies {Chase, 1998 #850} , for example 318, 100 and 300 cm-1 {Maroni, 1973 #11098}. CCSD(T)/atz calculations by Thanthiriwatte et al. provide harmonic frequencies of 324.9, 99.8 and 306.7 cm-1 {Thanthiriwatte, 2015 #11069}, unsurprisingly very close to our CCSD(T)/actz values of 325.9, 100.0 and 307.6 cm-1. Thus, simple estimates for ZPE are 359 cm-1 (half the experimental fundamentals), 365.7 cm-1 (harmonic from ref. {Thanthiriwatte, 2015 #11069}), and 366.8 cm-1 (our harmonic value). An anharmonic VPT2 calculation yields ZPE(PbCl2) = 366.2 cm-1 (and fundamental frequencies of 324.0, 99.6 and 305.8 cm-1), indicating a negligible effect from anharmonicity. The net change for reaction (2) is DZPE = (-26.1 ± 0.1) kJ/mol.

As stated earlier, the spin-orbit stabilization energy, *E*so cannot be measured experimentally. Theoretical values for the Pb, O, and PbO were presented above. Values of *E*so Cl2 and PbCl2 are approximated as their vertical values, here calculated to be -7.3 and ‑263.9 cm-1, respectively. A value of zero is assumed for H2 and H2O. To estimate the bias associated with the vertical approximation, we consider the PbO molecule. Our adiabatic value is *E*so = -1119 cm-1 and the corresponding vertical value is -978 cm-1. The adiabatic value is larger (in magnitude) by about 14 %. Thus, we increase our values for other molecules by 14 % as an estimated correction for the vertical bias. We estimate the associated standard uncertainty to be half this amount. The net change for reaction (2) is D*E*so = (-9.9 ± 0.3) kJ/mol.

Besides our approach of computing a value of *E*so for each species individually, one can compute a reaction energy relativistically {T. Saue, 2025 #11105;Saue, 2020 #3861}. The value of *E*so for the reaction is the difference between the reaction energy computed normally (with the default Dirac-Coulomb Hamiltonian) and computed with a spin-free Hamiltonian that excludes spin-orbit coupling {Dyall, 1994 #11083}. This was the approach used by Thanthiriwatte et al. to correct their high-quality non-relativistic reaction energies {Thanthiriwatte, 2015 #11069}. At the CCSD(T) level and using Dyall’s {Dyall, 2006 #1913} v3z basis sets (the largest that we could), we obtain a net value of *E*so = -9.8 kJ/mol for reaction (2). This is in good agreement with our species-specific approach.

The combined changes in CCSD(T) energy, ZPE and *E*so are D(2)*H*0 = (487.5 ± 2.3) kJ/mol. This corresponds to = (76.6 ± 2.6) kJ/mol, 10 kJ/mol higher than our inference from the dissociation energy.

**References**