



Prediction of vapor–liquid equilibria for the Pb–X (X=Ag, Cu and Sn) systems in vacuum distillation using ab initio methods and Wilson equation



XiaoMei Yang^{a, b}, XiuMin Chen^{a, c}, Cheng Zhang^c, XiaoGuang Xie^d, Bin Yang^{a, c}, BaoQiang Xu^{a, c}, DaChun Liu^{a, c}, HongWei Yang^{a, c, *}

^a The State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, 650093, PR China

^b College of Traditional Chinese Medicine, Yunnan University of Traditional Chinese Medicine, Kunming 650500, Yunnan, PR China

^c National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, 650093, PR China

^d School of Chemical Science and Technology, Yunnan University, Kunming, 650091, PR China

ARTICLE INFO

Article history:

Received 14 December 2015

Received in revised form

9 February 2016

Accepted 12 February 2016

Available online 13 February 2016

Keywords:

Vacuum metallurgy

VLE phase diagram

Ab initio methods

Wilson equation

ABSTRACT

In this work, interaction energies between pairs of atoms for the Ag–Pb, Cu–Pb and Sn–Pb systems have been calculated using ab initio methods. These energies are then used as the interaction energy parameters in the Wilson equation. Phase diagram of vapor–liquid equilibria (VLE) for the Pb-based alloy systems in vacuum distillation are obtained based on the calculated parameters. The results indicate that this approach can lead to accurate VLE predictions for alloy systems in vacuum distillation based only on properties of pure components and the structure of the clusters. The comparisons show the computational results are in good agreement with the experimental data.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Separation and purification of primary metals from nonferrous crude metals by vacuum distillation has been studied over past decades [1,2]. Reliable vapor–liquid equilibria (VLE) data are necessary for design and operation of separation processes for crude metals in vacuum distillation.

Activity coefficients are very important in phase equilibria calculations. The Wilson equation based on the concept of local composition which provides a very good representation of non-ideal mixtures [3]. Parameters for activity coefficient model such as Wilson equation are usually determined by regression of experimental data. But the experimental thermodynamic study is very time consuming and difficult. Therefore, theoretical predicting is a significant and effective approach to obtain thermodynamic

properties of alloys based only on properties of pure components and the structure of the atoms.

In our previous work, vacuum distillation experiments for Ag–Pb, Cu–Pb and Sn–Pb alloys were carried out [4–6]. Ab initio quantum mechanics methods provide a way to calculate the interaction energies between atoms [7]. The development of very efficient exchange–correlation functional in density functional theory (DFT) and the increasing computer power have made it possible to do computer simulations of great accuracy in a reasonable time.

In this paper, we use ab initio quantum mechanics methods to determine the parameters in the Wilson for Ag–Pb, Cu–Pb and Sn–Pb alloys. By determining the stable structure of the clusters of alloys in a condensed phase, the interaction energies between pairs of atoms in the cluster were calculated without the use of experimental data. The VLE phase diagrams of Pb-based alloy systems in vacuum distillation were predicted based on the Wilson equation and ab initio methods.

* Corresponding author. The State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, 650093, PR China.

E-mail address: hongweiy325@gmail.com (H. Yang).

Table 1
Interaction energies from ab initio calculations.

<i>i-j</i>	T	E_{ij} (kJ/mol)	E_{ji} (kJ/mol)	E_{ij} (kJ/mol)	Δu_{ij} (kJ/mol)	Δu_{ji} (kJ/mol)
Cu–Pb	1473	–64.677	–76.796	–54.843	21.953	9.834
Ag–Pb	1300	–43.145	–82.377	–55.929	26.448	–12.784
Sn–Pb	1050	–78.793	–72.496	–70.174	2.322	8.619

Table 2
Saturated vapor pressure experimental equations [17] and molar volumes [18] of Ag, Cu, Sn and Pb in liquid stated.

<i>i</i>	Vapor pressure equation (mm Hg)	Temperature (K)	V_{mi} (cm^3/mol)
Ag	$\lg p^* = -14400T^{-1} - 0.85 \lg T + 11.7$	1235–2435	$11.6 [1 + 0.98 \times 10^{-4} (T-234)]$
Cu	$\lg p^* = -17520T^{-1} - 1.21 \lg T + 13.21$	505–2875	$7.94 [1 + 1.0 \times 10^{-4} (T-135 + 6)]$
Sn	$\lg p^* = -15500T^{-1} + 8.23$	505–2875	$17.0 [1 + 0.87 \times 10^{-4} (T-505)]$
Pb	$\lg p^* = -10130T^{-1} - 0.985 \lg T + 11.6$	601–2022	$19.4 [1 + 1.24 \times 10^{-4} (T-600)]$

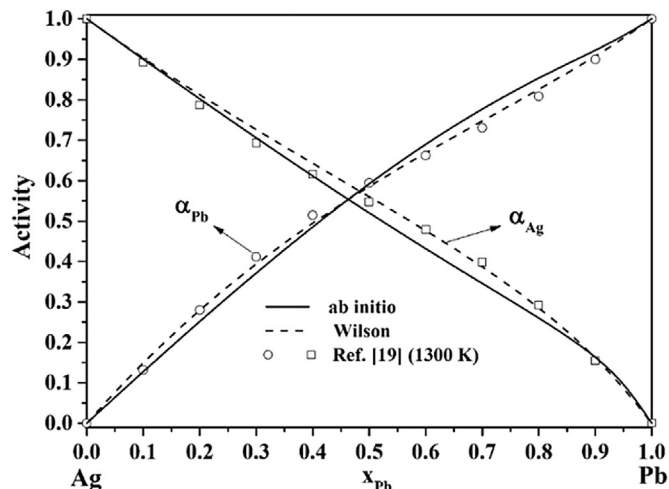
2. Computational procedure

The interaction parameters in the activity coefficient model is calculated by using the ab initio methods, and the method is as follows:

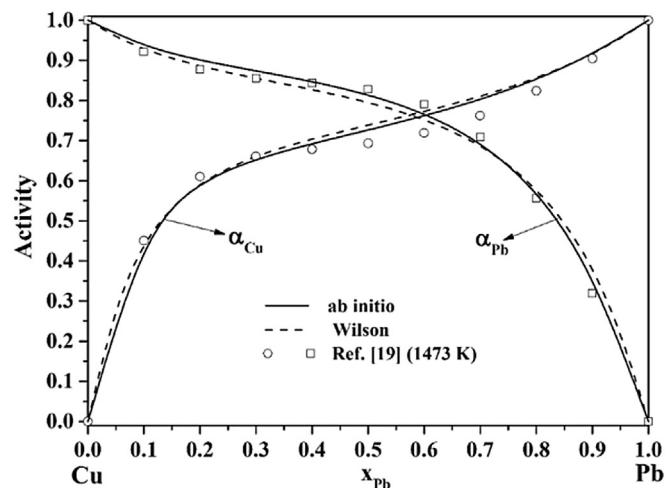
Firstly, we constructed the Pb_nM_n ($M = \text{Ag, Cu or Sn, } n = 2-12$) clusters, the number of Pb, M ($M = \text{Ag, Cu or Sn}$) atoms containing in the clusters are n . In order to obtain the stable structure of the clusters, the density functional theory (DFT) method was used to optimize the structures of the clusters. In this study, the DFT calculations were performed by using the program package Dmol³ in the Materials Studio software. Exchange and correlation effects were treated with generalized gradient approximation (GGA) implemented in the Perdew–Burke–Ernzerhof functional (PBE) as exchange–correlation functional [8,9]. The core treatment was all electron relativistic, the basis set was DNP, the convergence criteria for geometry optimization and energy calculation were energy tolerance of 1.0×10^{-6} eV/atom, maximum force tolerance of 0.02 eV/Å and maximum displacement tolerance of 0.005 Å.

In order to search the structure with global energy minimum for the calculation of interaction parameters, The ab initio molecular dynamics (AIMD) simulations were carried out on the optimized Pb_nM_n ($M = \text{Cu, Ag or Sn, } n = 2-12$) clusters, using the NVT ensemble at 300 K, a time step of 1 fs and the simulation time 10 ps [10–15]. The Massive GGM thermostat were used to control temperature [14]. The cluster configuration which has the lowest energy during the molecular dynamics process was used as the initial structure of the structure optimization, the DFT (GGA/HCTH) method was used to optimize the structure.

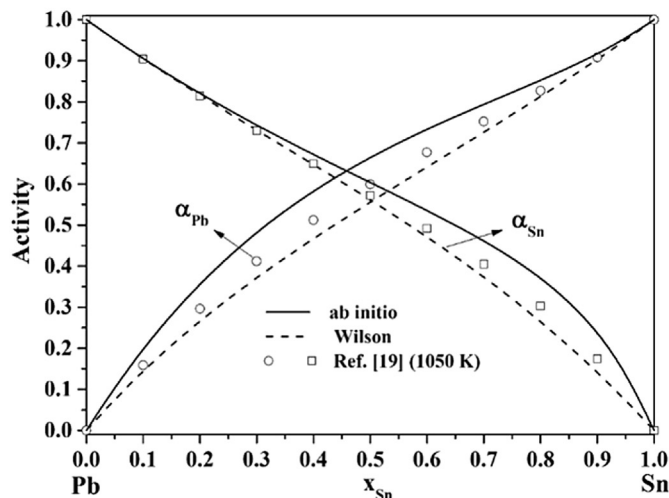
The atoms pairs of same atoms in the optimized clusters were selected, selected atoms pairs were treated as one of two subsystems involved in the BSSE(basis set superposition error) calculation, BSSE method in Dmol³ was used to calculate the interaction energy of atoms pairs in the cluster, (Exchange and correlation effects were treated with generalized gradient approximation (GGA) implemented in the Hamprecht, Cohen, Tozer and Handy functional (HCTH) as exchange–correlation functional [16]. The core treatment was all electrons relativistic, the basis set was DNP, and the convergence criteria for energy calculation were: (1) an energy tolerance of 1.0×10^{-6} eV/atom, (2) maximum force tolerance of 0.02 eV/Å and (3) maximum displacement tolerance of 0.005 Å. The pair interaction energy of binary mixture ij is



(a)



(b)



(c)

Fig. 1. Comparison of the predicted activities of ab initio (lines) with experimental data (symbols) and calculations by Wilson equation (dash lines) of alloys systems (a) Ag–Pb at 1300 K, (b) Cu–Pb at 1473 K and Sn–Pb at 1050 K.

Download English Version:

<https://daneshyari.com/en/article/200804>

Download Persian Version:

<https://daneshyari.com/article/200804>

[Daneshyari.com](https://daneshyari.com)