

Thermochemistry and modeling in oxides

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Abstract

In the present paper, taking examples in the Si–SiO₂ system, we show that thermodynamics still play a fundamental role in the understanding of the microscopic behavior of materials. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction: goal of the present paper

Thermodynamics has long been a way to access a microscopic understanding via the methods of statistical thermodynamics following the work of Fowler and Guggenheim [1]. The calorimetric determination of partial molar enthalpy of mixing of oxygen [2] or of hydrogen [3] is in fact a way to measure the energy of formation of interstitial atoms in metals or of oxygen and hydrogen vacancies in oxides and hydrides. The variation of the partial molar enthalpy with composition allows to evaluate interaction energies. These interactions may be short range [4] or coulombic long range [5].

In view of the impressive progress of *ab initio* calculations available for complex systems [6–8] and of the availability of more and more sophisticated experimental methods one can wonder if thermodynamics which averages everything is still of some help in the microscopic understanding of materials. In our opinion, the answer is clearly positive. We shall discuss essentially the use of enthalpies rather than the use of phase diagrams: as discussed elsewhere [9], the use of reliable values of partial molar enthalpies and entropies [10] is much more reliable than the use of phase diagrams to build a model.

The goal of this paper is to show how in this context information obtained from thermodynamics can be used to

improve our knowledge of microscopic properties. We shall restrict ourselves to examples met in the recent work of the authors which is related to the Si–SiO₂ system.

2. The Si–SiO₂ system

The calculation of the energy of formation of an insulated defect in a solid is a difficult problem of *ab initio* methods. We have to choose from several types of methods:

- Use of embedding codes in the framework of the density functional [11] or of the Hartree–Fock approximation [12].
- Cluster calculations performed within post Hartree–Fock methods including correlation [13].
- Supercells with periodic boundary conditions in the framework of the density functional [14] or of the Hartree–Fock approximation [15].

Let us consider the case of the formation of an oxygen vacancy in silica. It is an important problem as these defects are expected to be found at the Si–SiO₂ interface [16] which is of prime importance in the electronics industry. So a large number of semi-empirical and *ab initio* methods have been used and provide largely scattered values. And there is no obvious way to decide which is the correct value as all the *ab initio* calculations use approximations:

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- Limited basis and lack of correlation in embedded Hartree–Fock calculations.
- Lack of long range effects and crystal periodicity in cluster calculations.
- Ultrasoft potentials and small supercells in density functional calculations.

Fortunately, thermodynamics can help us to make a choice [17], even if direct measurements are out of reach. After some animated discussions [18–20], a reliable value of the enthalpy of formation of α -quartz has become available ([21], $-910.7 \pm 1 \text{ kJ mol}^{-1}$). The Gibbs–Helmholtz relation allows one to conclude that the energy of formation of an oxygen vacancy in α -quartz (with the molecular dioxygen as reference state) has to be larger than 4.7 eV [17]. Two recent studies [13,22] have allowed one to obtain values in agreement with the thermodynamic criterion, which allows one to draw some conclusions concerning the theoretical treatment of defects in silica:

- Correlation and d orbitals are mandatory in Hartree–Fock treatments [13].
- Cluster calculations provide a good approximation, which means that long range effects are of no importance.
- Calculations based on the density functional theory (DFT) using the generalized gradient approximation (GGA) for the exchange correlation provide results in close agreement with cluster calculations.

This approach has also allowed one to obtain a simple explanation for a puzzling observation concerning the Si–SiO₂ interface [23]: an activation process (photoionization or trapping of radiation-induced free carriers) allows one to promote neutral oxygen vacancies into defects harboring an unpaired electron spin (E' centers). EPR measurements can thus be used to measure the number of these defects in the vicinity of the interface. Generally, experimental results are rationalized with an Arrhenius plot allowing one to define an activation energy. This activation energy is found to be equal to 1.5 eV [24]. The simplest modeling track is to identify this activation energy with the enthalpy of formation of an oxygen vacancy. But the measured activation energy is much lower than the lower bound imposed by thermodynamics (4.7 eV) and than recent theoretical calculations [13,22]. This discrepancy disappears if we assume that we have a local equilibrium between the silicon and the silicon dioxide. The oxygen vacancy population is the population of substoichiometric silica in equilibrium with the two-phase Si–SiO₂ domain. In this case, the activation energy is related to the slope of the phase boundary between the small SiO_{2-x} domain and the large two-phase Si–SiO₂ domain. A vertical boundary would lead to a zero activation energy. It can easily be shown [23] by a purely thermodynamic reasoning that the activation energy is nothing else than half the difference between the partial molar enthalpy of mixing of oxygen $\Delta H(\text{O}_2)$ in silica (which may be computed as discussed

above) and $\Delta_f H_T^0(\text{SiO}_2)$ the enthalpy of formation of silica which is known with a good accuracy [21]. Our calculation provides a value of 1.3 eV in excellent agreement with the experimental value.

3. Summary and conclusion

In spite of the impressive success of modern experimental and theoretical methods, thermodynamics remains an invaluable way to ensure the consistency of different approaches. Let us conclude with a citation of the second edition of the classical article of Lewis and Randall revised by Pitzer and Brewer [25]:

The fascination of a growing science lies in the work of the pioneers at the very borderland of the unknown, but to reach this frontier one must pass over well-traveled roads; of these one of the safest and surest is the broad highway of thermodynamics.

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