

# Effect of Oxygen Concentration on the Solution Enthalpy of Fe in Liquid Na: A First-principles Study

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## 1. Introduction

In order to safely and efficiently use liquid Na as a coolant in advanced fast reactors, there are several material issues to be deeply understood, such as material corrosion and transport of radioactive impurity. Although liquid Na has advantages over material integrity compared to other liquid metal candidates such as liquid Pb and Pb-Bi eutectic, the knowledge of long-term corrosion of structural materials is still limited. It is also difficult to track the behavior of radioactive impurities in liquid Na at elevated temperatures. To accurately predict the behavior of radioactive impurities in any situation can help develop appropriate safety regulation and measures to protect plant workers, the public, and the environment from radiation exposure.

The thermodynamic properties that directly affect the corrosion rate of structural materials and the transport of radionuclides are solubility and diffusivity. However, inter-impurity interactions make the measurement through experiments complicated and difficult. For example, Fe solubility in liquid Na is known to differ by four orders of magnitude among experiments depending on the O concentration [1]. Numerous types of inter-impurity interactions are expected to be present in liquid Na of advanced fast reactors. Hence, examining the effect of all types of inter-impurity interactions on solubility and diffusivity through experiments is difficult and expensive in cost and time.

As an alternative method estimating the thermodynamic properties, quantum mechanical calculations based on density functional theory (DFT) have been widely utilized. The ultimate goal of our studies is to make a model using the equilibrium and rate theory so as to consider the effect of inter-impurity interactions on the solubility of two arbitrary elements in liquid Na. To this end, this study aims to make and evaluate a model considering the effects of O-Fe and Fe-Fe interactions on the Fe solubility in liquid Na.

## 2. Computational details

First-principles molecular dynamics (FPMD) simulations of liquid Na systems were performed using DFT as embedded in the Vienna *ab initio* simulation package (VASP) code [2]. The Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) was used to evaluate the exchange-correlation energy. For Na, Fe, and O, the valence electrons of  $3s^1$ ,  $3d^64s^2$ , and  $2s^22p^4$  were used,

respectively, which were represented by plane waves with an energy cutoff of 500 eV. The effects of the core electrons were dealt with by the projected augmented wave (PAW) method. The band energy was calculated over a  $2 \times 2 \times 2$  Monkhorst-Pack grid in the Brillouin zone, using the first order Methfessel-Paxton smearing method with 0.2 eV smearing width. The convergence criterion of a self-consistent field calculation was set to  $10^{-6}$  eV per system energy. The spin-polarization was considered for all systems.

FPMD simulation of the liquid Na system composed of 102 atoms, was performed for 20 ps with 1.2 fs time-step under a canonical ensemble (NVT) with the system temperature of 1000 K. After the simulation, a Na atom was replaced with Fe or O atom, respectively. Then, another 30 ps simulations were performed. Subsequently,  $FeO_n$  ( $n=1\sim4$ ) were prepared by adding an O atom near the Fe atom dissolved in liquid Na.  $Fe_2O_m$  ( $m=1\sim3$ ) and  $Fe_k$  ( $k=2\sim4$ ) were prepared by replacing a Na atom with Fe atom near  $FeO_n$  or adding an Fe atom near  $Fe_k$ , respectively. Each liquid system contains an impurity atom or a compound, so inter-impurity and inter-compound interactions were not considered in this study. Subsequent 10 ps simulations were performed for all tested systems. To increase the statistical accuracy of the simulation results, two independent FPMD simulations with different initial configurations were performed. When a compound dissociates during the FPMD simulations, we discarded the data and initiated the simulation again with a different initial configuration. The first 4 ps simulation data for each system was abandoned and the rest was used for data production.

The quasi-harmonic approximation (QHA) calculation combined with the calculation results of DFT was performed by phonopy code [3] to estimate a finite temperature enthalpy of bcc-Fe considering the effect of the lattice vibration. In detail,  $4 \times 4 \times 4$  supercells were prepared having a different lattice constant from 97% to 103% at 0.5% interval from the equilibrium lattice constant. After making an atomic displacement of approximately 0.01 Å, static calculation was performed. Then, thermodynamic values such as enthalpy were estimated by phonopy code [2] based on the dynamic matrix constructed by atomic force information calculated with DFT.

## 3. Results and discussion

### 3.1 Solution enthalpy of Fe in liquid Na

The solution enthalpy of Fe,  $H_{Sol}$ , refers to the amount of enthalpy needed for Fe atom to dissolve from bcc-Fe to liquid Na. In experiment,  $H_{Sol}$  is equal to the slope of the relation between solubility and reciprocal of temperature. In calculation, the solution enthalpy of Fe in liquid Na can be described as follows:

$$H_{Sol} = H_{Liq.Mixture} - (H_{Pure-Liq.Na} + H_{Fe-crystal}), \quad (1)$$

where  $H_{Liq.Mixture}$ ,  $H_{Pure-Liq.Na}$ , and  $H_{Fe-crystal}$  are the enthalpies of Fe-containing and pure Na systems and per-atom enthalpy of bcc-Fe at 1000 K, respectively. Fig. 1 describes the enthalpy diagram for analyzing Fe solution enthalpy in liquid Na. The liquid enthalpy at 1000 K was evaluated by averaging the enthalpy, which is the sum of potential and kinetic energy, over all trajectories of the simulation. The crystal enthalpy was estimated by performing the QHA calculation. The Fe solution enthalpy in liquid Na was finally calculated to be approximately 2.81 eV.

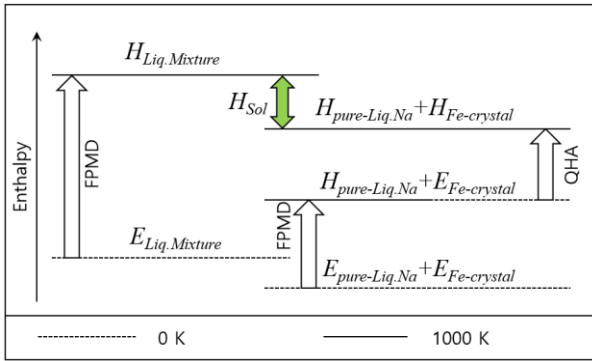


Fig. 1. Enthalpy diagram for analyzing the solution enthalpy of Fe in liquid Na at 1000 K.

### 3.2 Chemical equilibrium for Fe solubility

The chemical equilibrium is often used in materials science to describe the equilibrium thermodynamic properties of phases or reactions in terms of free energy. For simplicity, we first assume that only Fe atom (not Fe-oxides, not Fe-clusters) can be dissolved in liquid Na in this Section. This assumption indicates that the formation of Fe-clusters and Fe-oxides is not considered in this model. It can be imagined that there is an arbitrary large system of bcc-Fe in direct contact with liquid Na at 1000 K. If the number of bcc-Fe atoms, Fe atoms dissolved in liquid Na, and liquid Na atoms are defined as  $N_{s,Fe}$ ,  $N_{l,Fe}$  and  $N_{Na}$ , respectively, the Gibbs free energy of the arbitrary system can be written as a function of  $N_{l,Fe}$  as follows:

$$G(N_{l,Fe}) = (N_{s,Fe}h_{s,Fe} + N_{l,Fe}h_{l,Fe}) - T(S_{config} + N_{s,Fe}S_{s,Fe} + N_{l,Fe}S_{l,Fe}), \quad (2)$$

where  $h_{s,Fe}$  and  $h_{l,Fe}$  are the per-atom enthalpy of Fe atom in bcc-Fe and liquid Na, respectively.  $S_{config}$  is the configurational entropy.  $S_{s,Fe}$  and  $S_{l,Fe}$  are the per-atom entropy other than configurational terms of Fe in bcc-Fe and liquid Na, respectively. If  $h_{s,Fe}$  is taken as the reference enthalpy, 0 eV,  $h_{l,Fe}$  stands for the calculated

Fe solution enthalpy in liquid Na, 2.81 eV.

The system equilibrium is achieved as the first-derivative of the Gibbs free energy with respect to  $N_{l,Fe}$  becomes zero. This relation gives us the equilibrium solubility of Fe in liquid Na as follows:

$$\frac{N_{l,Fe}}{N_{Na}} = \exp\left(-\frac{h_{l,Fe} - T(S_{l,Fe} - S_{s,Fe})}{k_B T}\right). \quad (3)$$

$S_{s,Fe}$  is evaluated by performing QHA calculation. Due to difficulty in evaluating entropy of Fe in liquid Na by the calculation,  $S_{l,Fe}$  was assumed to be very similar to the experimental entropy of Na atom in liquid Na [4].

Fig. 2 presents the solubility of Fe in liquid Na evaluated using the chemical equilibrium model and the calculated solution enthalpy. The slope of the graph is equal to the calculated Fe solution enthalpy. However, the slope and solubility were much larger and smaller than those of experimental values, respectively. The main causes of the mismatch are thought to be non-negligible effects of Fe-clusters and Fe-oxides formation on Fe solubility in experiments. In addition, the energy calculated by DFT-GGA functional may be erroneous. Therefore, to decrease the mismatch between results and experiments, the effects of Fe-clusters and Fe-oxides formation on solubility are discussed in Section 3.3 and appropriate DFT-error correction method is suggested in Section 3.4, respectively.

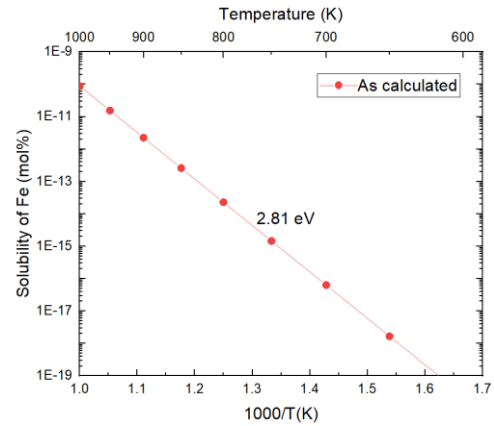


Fig. 2. The calculated solubility of Fe in liquid Na at 1000 K using the chemical equilibrium model and DFT results.

### 3.3 Rate theory for effective Fe solubility

To further consider the effect of Fe-clusters and Fe-oxides formation on Fe solubility in liquid Na, a model using the rate theory was developed. First, we describe simple examples of the developed rate equations for FeO and FeO<sub>2</sub> formation in liquid Na, as shown in Fig. 3(a) and (b), respectively. For FeO formation, if O atom is located near the Fe atom with a probability related to O concentration ( $N_O/N_{Na}$ ), and overcomes the enthalpy barrier of  $H_I$  with the O frequency ( $\nu_O$ ), then FeO molecule can be formed in liquid Na. Reversibly, FeO can dissociate if O atom overcomes the enthalpy barrier

of  $H_2$  with  $v_O$ . Thus, the rate equation can be written as follows:

$$N_{Fe} \eta \frac{N_O}{N_{Na}} v_O \exp\left(-\frac{H_1}{k_B T}\right) = N_{FeO} v_O \exp\left(-\frac{H_2}{k_B T}\right), \quad (4)$$

where  $\eta$  is a geometric factor, which indicates the number of 2<sup>nd</sup> neighboring atoms that are likely to jump to the 1<sup>st</sup> neighboring atoms of Fe or Fe-clusters/oxides. The geometric factor and enthalpy difference ( $H_1$ - $H_2$ ) are estimated by FPMD simulations. Since the steady-state approximation was applied in this study, the difference in enthalpy barrier was used instead of the absolute value of  $H_1$  and  $H_2$ . Therefore, the balance of the reactants and products determines the concentration of FeO ( $N_{FeO}/N_{Na}$ ) in liquid Na.

Subsequently, the rate equation for estimating the concentration of FeO<sub>2</sub> ( $N_{FeO_2}/N_{Na}$ ) can be established as follows:

$$N_{FeO} \eta \frac{N_O}{N_{Na}} v_O \exp\left(-\frac{H_3}{k_B T}\right) = N_{FeO_2} 2v_O \exp\left(-\frac{H_4}{k_B T}\right). \quad (5)$$

In the similar way, if O atom is located near the Fe side of FeO molecule with a probability related to O concentration and overcomes the enthalpy barrier of  $H_3$  with  $v_O$ , the FeO<sub>2</sub> molecule can be formed. Reversibly, FeO<sub>2</sub> can dissociate if one of the two O atoms overcomes the enthalpy barrier of  $H_4$  with  $v_O$ .

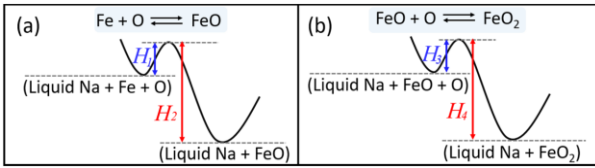


Fig. 3. Schematic illustration for explaining FeO and FeO<sub>2</sub> solubility evaluation by the rate theory.

Likewise, the rate equations can be made to determine the concentration of Fe-oxides and Fe-clusters such as FeO<sub>n</sub> (n=1~4), Fe<sub>2</sub>O<sub>m</sub> (m=1~3), and Fe<sub>k</sub> (k=2~4) in liquid Na.

### 3.4 Correction by the DFT calculation error

The DFT-PBE functional often fail to predict the energy of Fe-oxide molecules. Namely, there is a possibility that DFT-calculated enthalpy of liquid Na containing Fe-oxide or Fe-cluster is erroneous. Therefore, it is necessary to use an appropriate correction method for the calculated enthalpy.

Since the chemical state of Fe in liquid Na is very similar to that in a vacuum [5], it is assumed that the chemical states of Fe-oxides and Fe-clusters in liquid Na are also similar to those in a vacuum. Then, it can be suggested that the calculation error of the compound in liquid Na is at the same level as a vacuum.

For instance, Fig. 4 describes the correction method for FeO<sub>2</sub> molecule. If we take the atomic energy as a reference level in a vacuum, there is a 1.35 eV FeO<sub>2</sub> molecule energy difference between the calculation and

the experiment [6]. We suggest that this error can occur with the same level in the liquid Na system. If the DFT-calculated enthalpy of liquid Na containing Fe or O atom is assumed to be correct, then the error in enthalpy of liquid Na containing FeO<sub>2</sub> molecule should be 1.35 eV, which was used to correct the enthalpy barriers in Eq. (5). In the same way, the differences in enthalpy barrier were corrected for all Fe-oxides and Fe-clusters.

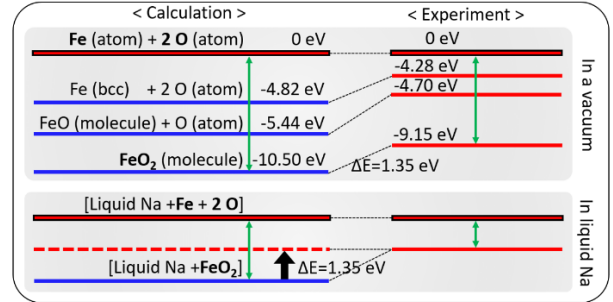


Fig. 4. Energy diagram for explaining correction method for FeO<sub>2</sub> molecule in liquid Na, as an example.

### 3.5 Effective solubility of Fe

Based on the corrected enthalpy, the effective solubility of Fe considering the formation of Fe-oxides and Fe-clusters were calculated by solving the equilibrium and rate equations described in Section 3.2 and 3.3, respectively. Fig. 5 presents the effective Fe solubility with different O concentrations. It can be seen that the slope, which is the effective Fe solution enthalpy, decreases from 2.27 eV to 0.80 eV when increasing the O concentration in liquid Na. The calculated results at a high O concentration of 10<sup>-1</sup> mol% is well consistent with the recommended experimental Fe solubility [1] shown as the black line in Fig. 5.

It was further revealed that the Fe-clusters such as Fe<sub>2</sub> and Fe<sub>3</sub> are rarely formed in liquid Na. Since the solubility of Fe<sub>2</sub> and Fe<sub>3</sub> is much lower than that of Fe, it can be deduced that Fe-clusters with more than 4 Fe atoms are also expected to be hardly soluble in liquid Na, whereas Fe-oxides such as FeO<sub>2</sub> and FeO<sub>3</sub> are readily formed in liquid Na.

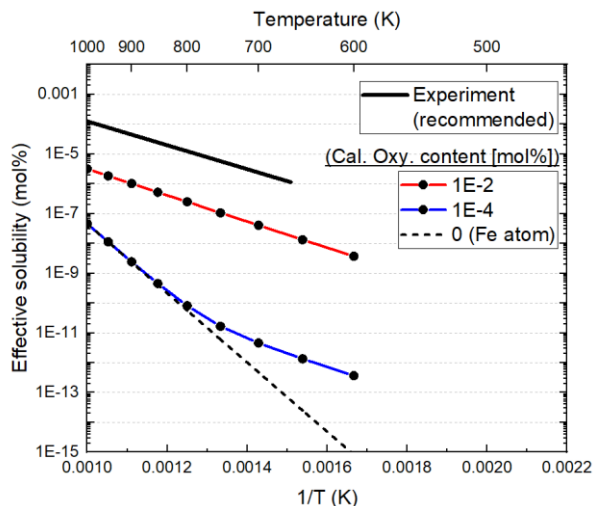


Fig. 5. The effective Fe solubility in liquid Na considering the formation of Fe-oxides and Fe-clusters.

#### 4. Conclusions

A method for evaluating the effective Fe solubility considering the formation of Fe-clusters and Fe-oxides in liquid Na has been suggested using the equilibrium and rate theory based on the results of first-principles calculations. A correction method has been proposed to overcome the drawbacks of molecular energy calculation by DFT-PBE functional. We found that the calculated Fe solution enthalpy of 2.27 eV decreases to 0.80 eV when considering the formation of Fe-clusters and Fe-oxides, which nicely agrees with the experimental value of 0.81 eV. It was additionally found that the Fe-oxides and Fe-clusters are highly and rarely formed in liquid Na, respectively.

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