

Evaluation of solution enthalpy for key gaseous impurities in liquid sodium by quantum mechanical calculations

Junhyoung Gil and Takuji Oda*

Department of Energy Systems Engineering, Seoul National University, Seoul 08826

*E-mail: oda@snu.ac.kr

1. Introduction

In a sodium-cooled fast reactor (SFR), the transport behavior of impurities, especially some radionuclides, in liquid sodium must be carefully and comprehensively understood to achieve the reactor safety and radiation safety. Solubility is one of the fundamental transport properties of impurities. However, it is often difficult to be determined by experiments partly because of the high chemical reactivity of liquid sodium with water and air and the difficulty in the purity control of liquid sodium.

Quantum mechanical (QM) calculations based on the density functional theory (DFT) can be an alternative to determine the solubility of impurities. In our previous study [1], the performance of several DFT exchange-correlation functionals for liquid sodium simulations was assessed. As a result, the Perdew-Burke-Ernzerhof (PBE) [2] of generalized gradient approximation (GGA) [3] functionals exhibited good performance in terms of liquid sodium simulations.

In the present study, by conducting QM calculations using the PBE functional, solution enthalpies for some key gaseous impurities, namely O₂, H₂, and I₂, in liquid sodium are evaluated. Oxygen impurity can react with sodium to form Na₂O that may cause channel blockage in the heat exchanger, and can react with steels to accelerate corrosion. The leakage of tritium, a radioisotope of hydrogen, through structural materials made of Fe-Cr alloys is a radiation safety concern. Iodine is a volatile radionuclide that can be released during accidents.

To evaluate thermodynamic quantities, first-principles molecular dynamics (FPMD) simulations are performed for pure and impurity-including liquid sodium systems. For gaseous species, vibration analysis based on the potential energy curve obtained from QM calculations is conducted. The calculated solution enthalpies are compared to available experimental data to check the accuracy of the calculation results.

2. Models and Methods

2.1. Model liquid sodium system

A cubic supercell consisting of 102 Na atoms is prepared as a model pure sodium system. The volume of the supercell is determined from our previous study of liquid sodium [1] where the volume giving 0 Pa as the internal pressure was estimated by varying the system volume. For the simulations of condensed matters, a 0-Pa pressure is virtually equivalent to the atmospheric

pressure. The initial atomic configuration is prepared from our previous study of liquid lead-bismuth eutectic (LBE) [4], considering that both liquid sodium and LBE atoms interact in an isotropic manner.

From a pure sodium system, one randomly selected Na atom is replaced to an impurity atom to prepare a model impurity-including sodium system. The system volume is maintained the same as that of the pure sodium system because only one Na atom is replaced. Because only one impurity atom is involved in the simulation cell under the periodic boundary conditions, the distance between impurity atoms cannot become less than a cell constant (around 16.461 Å at 600 K). This means that the interaction among impurity atoms is not considered in the present study.

2.2. FPMD simulation

For a pure sodium system, FPMD simulations are performed for 25 ps at the temperatures of 600 K and 1000 K. These two temperatures are chosen considering the melting point and boiling point of sodium. The initial 5-ps data is discarded as an equilibration run. To improve the statistics, three independent simulations starting with different initial atomic configurations are performed at each temperature. Thus, in total, 60-ps FPMD data is analyzed at each temperature.

For an impurity-including sodium system, FPMD simulations are performed for 55 ps at 600 K and 25 ps at 1000 K. Longer simulations are performed at 600 K to estimate diffusion coefficients of the impurities in liquid sodium in a follow-up study. Similarly to the pure sodium system, the initial 5-ps data is discarded as an equilibration run, and three independent simulations with different initial configurations are performed. Thus, in total, 150-ps and 60-ps FPMD data are analyzed at 600 K and 1000 K, respectively.

Simulations are performed using the VASP code [5] with the utilization of the GGA-PBE functional [2, 3] to evaluate the exchange-correlation energy. The valence electron configuration for each element is listed in Table 1. The electronic wave functions of the valence electrons are represented by plane waves with the energy cutoff of 400 eV. The effects of core electrons including the scalar relativistic effect are modeled by the projector augmented wave (PAW) method [6, 7]. The band energy is sampled over a 2×2×2 Monkhorst-Pack grid [8] resulting in four irreducible k-points, with the Methfessel-Paxton smearing scheme of the first order [9] with a 0.2-eV smearing width.

Table 1. Valence electron configuration for each element.

Element	Valence electron configuration
Na	3s ¹
O	2s ² 2p ⁴
H	1s ¹
I	5s ² 5p ⁵

2.3. Vibration analysis

According to the statistical thermodynamics [10], thermodynamic quantities of gaseous molecules can be obtained from the partition function Z for gases:

$$Z(N, V, T) = \frac{[q(V, T)]^N}{N!} \quad (1)$$

$$q(V, T) = q_{trans} q_{rot} q_{vib} q_{elec}$$

where N is the number of molecules, V (m³) is the system volume, T (K) is the system temperature, and q is the partition function for a gas molecule with q_{trans} , q_{rot} , q_{vib} , q_{elec} being translational, rotational, vibrational, and electronic components, respectively.

Assuming that a system has a low pressure and a high temperature, gases can be treated as ideal gases without sacrificing accuracy. In addition, by applying the harmonic approximation to a diatomic molecule, e.g. O₂, H₂, and I₂, the expression for each partition function component can be simplified. Accordingly, the internal energy E (J/mol) and entropy S (J/K/mol) of a system are written as follows:

$$E = -\frac{\partial \ln Z}{\partial \beta} = \left\{ \frac{3}{2} Nk_B T \right\} + \left\{ Nk_B T \right\} + \left\{ Nk_B \left[\frac{\Theta_{vib}}{2} + \frac{\Theta_{vib} e^{-\Theta_{vib}/T}}{1 - e^{-\Theta_{vib}/T}} \right] \right\} + \left\{ -ND_e \right\}$$

$$S = \frac{\partial}{\partial T} (k_B T \ln Z) = \left\{ Nk_B \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{\bar{V} e^{5/2}}{N} \right] \right\} + \left\{ Nk_B \ln \frac{T e}{2\Theta_{rot}} \right\} + \left\{ Nk_B \left[-\ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} \right] \right\} + \left\{ 0 \right\}, \quad (2)$$

$$\beta = \frac{1}{k_B T}, \quad \Theta_{vib} = \frac{h\nu_h}{k_B}, \quad \Theta_{rot} = \frac{h^2}{8\pi^2 I k_B}, \quad I = \mu r_e^2, \quad \bar{V} = RT / P$$

where k_B is the Boltzmann constant, Θ_{vib} (K) is the vibrational temperature, D_e (J) is the binding energy of a molecule, m (kg) is the mass of a molecule, h is the Planck constant, Θ_{rot} (K) is the rotational temperature, ν_h (Hz) is the vibration frequency of a harmonic oscillator, I is the moment of inertia (kg·m²), μ (kg) is the reduced mass, r_e (m) is the equilibrium bond distance, and P (Pa) is the system pressure.

Finally, the enthalpy H (J/mol), Helmholtz energy A (J/mol), and Gibbs energy G (J/mol) are derived from the fundamental relations for thermodynamic quantities:

$$H = E + P\bar{V}$$

$$A = -k_B T \ln Z = E - TS \quad (3).$$

$$G = H - TS = A + P\bar{V}$$

From the QM calculations using the VASP code, D_e and r_e for each impurity molecule are determined. Next, ν_h is obtained by solving a one-dimensional Schrodinger equation and applying the harmonic approximation. With these quantities obtained, the internal energy, entropy, enthalpy, and free energy of the impurity molecules are evaluated at a given temperature based on the above expressions.

3. Results and Discussions

In this paper, only the calculation results for the solution enthalpy of oxygen in liquid sodium at 600 K are presented. The results at 1000 K and the results for the other impurities are to be discussed in the presentation.

3.1. FPMD results for pure liquid sodium

Table 2 lists the average energy and pressure for pure liquid sodium systems at 600 K. Because the average pressure for each system is non-zero, the energy needs to be corrected to the value corresponding to zero pressure. For this correction, the pressure-energy relation for system-1 was investigated. Specifically, six systems with the cell constants varying from the original value by $\pm 0.35\%$, $\pm 0.7\%$, and $\pm 1.0\%$ were simulated for 25 ps each. For each system, the first 5-ps data was discarded as an equilibration run. Subsequently, the data points were fitted by a 2nd-order polynomial, from which the energy correction to the zero pressure was made for each system. The correction results are summarized as zero-pressure energy in Table 2.

Table 2. FPMD results for pure liquid sodium systems simulated at 600 K.

System number	1	2	3
Energy (eV)	-112.654	-112.604	-112.728
Pressure (kBar)	-0.031	-0.010	-0.066
Zero-pressure energy (eV)	-112.669	-112.609	-112.761
Average over systems (eV)	-112.680 \pm 0.042		
Enthalpy (eV)	-112.677 \pm 0.042		

An average zero-pressure energy over three systems with a standard error is given in Table 2. The standard error was evaluated from the standard deviation of the energy data for each system with considering statistical inefficiency [11]. Finally, the enthalpy of the pure liquid sodium system at 600 K was obtained by adding the PV term to the energy. Because the energy was corrected to have the system pressure zero, the pressure and volume used are atmospheric pressure and the system volume.

3.2. FPMD results for O-including liquid sodium

For the O-including liquid sodium systems, because one Na atom was replaced to an O atom, system pressures were measured to be further from zero compared to the pure sodium cases. Assuming that the pressure-energy relation of O-including sodium systems is comparable to that of pure sodium systems, the energy values of the O-including sodium systems were corrected using the relation obtained from the pure sodium system. As a result, the average energy over three independent O-including sodium systems at 600 K was evaluated to be -120.096 ± 0.033 eV, with the corresponding enthalpy of -120.093 ± 0.033 eV.

3.3. Vibration analysis results for oxygen molecule

Figure 1 shows the potential energy curve of an oxygen molecule obtained from the QM calculations. By solving a Schrodinger equation regarding this curve, the binding energy (D_e), equilibrium bond distance (r_e), harmonic vibration frequency (ν_h), etc. were calculated. Using these data, the enthalpy of an oxygen molecule was evaluated, as shown in Figure 2. The results show an almost perfect agreement with the experimental data [12].

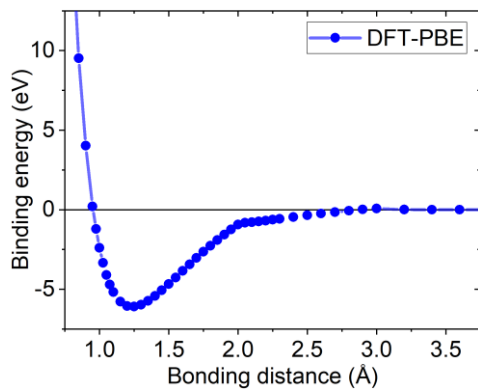


Figure 1. Potential energy curve obtained from DFT calculations using PBE functional.

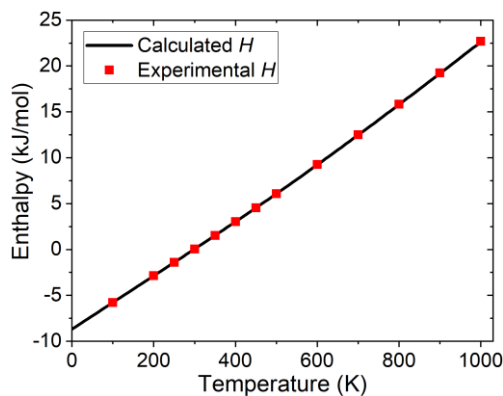


Figure 2. Calculation results for enthalpy of oxygen molecule, shown with experimental data for comparison.

3.4. Comparison with experimental data

Figure 3 shows an enthalpy diagram to compare the calculation results with experimental data. While the main result of this study corresponds to process-①, experimental data [13] is available for the Na_2O solution enthalpy corresponding to process-②. Thus, for comparison, additional QM calculations were performed for solid sodium and sodium oxide to evaluate the thermodynamic quantities of these two solids using the phonopy code [14].

First, the results for pure sodium, sodium oxide, and oxygen were compared with experimental data [12]. In Figure 3, for example, 23.3 kJ/mol for sodium was calculated from the enthalpy difference between solid sodium at RT and liquid sodium at 600 K. Overall the results showed a good agreement with experimental data, with the maximum error of 5.9 kJ/mol for the formation enthalpy of solid sodium oxide.

Regarding the solution enthalpy of Na_2O in liquid sodium, corresponding to process-②, the calculation result (11.6 kJ/mol) turned out to underestimate the experimental data (46.9 kJ/mol) by 35.3 kJ/mol, which is relatively large. However, the errors in the other quantities listed in Figure 3 including the solution enthalpy of O_2 in liquid sodium were acceptably small.

The results indicate that the error of QM calculations for the solution enthalpy in liquid sodium is in the order of a few tens of kJ/mol. Thus, if a solution enthalpy is large (> 100 kJ/mol), QM calculations can be used to evaluate the solution enthalpy. On the other hand, if it is small, the application of QM calculations requires careful consideration. Because experiments are easier if a solution enthalpy is smaller, QM calculations and experiments can be used complementarily to evaluate the solution enthalpy of impurities in liquid sodium.

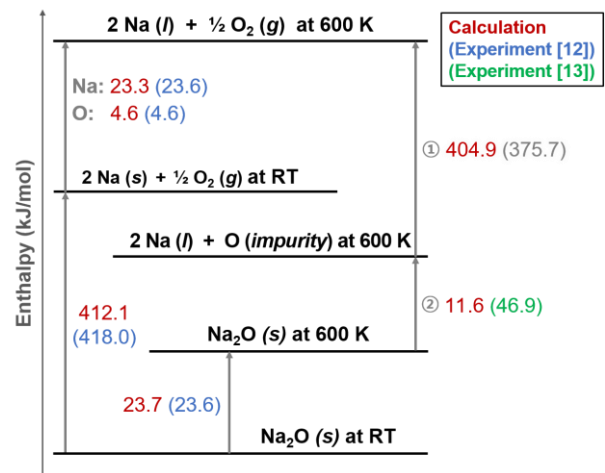


Figure 3 Enthalpy diagram to compare calculation results with experimental data. Process-① is the main results of this study while process-② corresponds to the experimental data for Na_2O solution enthalpy in sodium.

4. Conclusion

In the present study, the solution enthalpy of O₂, H₂, and I₂ in liquid sodium was evaluated using the QM calculations. The FPMD simulations were conducted for pure and impurity-including liquid sodium, and the vibration analysis was performed for gaseous impurities. For validation, the calculation results were compared with the available experimental data. In the case of oxygen, the error between the calculation results and the experimental data was measured to be acceptably small.

While the QM calculations and experiments are expected to be conducted complementarily for the evaluation of the solution enthalpy of impurities in liquid sodium, it is thought that the error between the calculation and the experimental results can be reduced if the evaluation process for the enthalpy of an impurity-including sodium system is more carefully examined. Focusing on this issue, discussions on the several possible causes of the error and how to reduce the error are to be held in the presentation.

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