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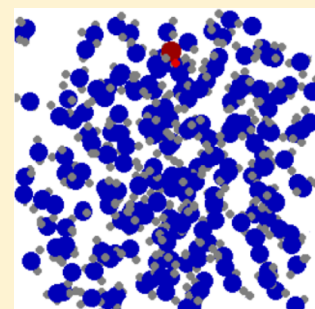
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# High Temperature Diffusion Coefficients for O<sub>2</sub>, H<sub>2</sub>, and OH in Water, and for Pure Water

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**ABSTRACT:** Classical molecular dynamics simulations using simple point charge water potential were performed to obtain high temperature diffusion coefficients for pure water, and for O<sub>2</sub>, H<sub>2</sub>, and OH radical in an infinitely dilute aqueous solution. The simulations were carried out at temperatures ranging from ambient to 973 K and system densities from 0.1 to 1.0 g cm<sup>-3</sup>. A logarithmic density expansion of a hard sphere collision model was used to formulate a polynomial fit to the diffusion data and four sets of fitting coefficients are presented. Fourteen coefficients were sufficient to accurately reproduce mass transport coefficients in water at high temperatures and at supercritical conditions. Our parametric fits can be used to estimate diffusion coefficients for these species in a wide range of thermodynamic states, including those relevant to the GEN IV supercritical water cooled nuclear reactor.



## 1. INTRODUCTION

Over the recent years much interest has been invested in the properties of high temperature and supercritical water. The thermodynamics, hydration, and transport properties of aqueous systems at these conditions are of importance for a variety of applications ranging from power generation to hazardous waste recycling, and in the study of geological processes such as carbon dioxide capture and sequestration.<sup>1–9</sup> Supercritical water holds promise as the thermodynamically favorable medium as both neutron moderator and heat transfer fluid in the GEN IV supercritical water cooled nuclear reactor (SCWR).<sup>10–14</sup> The lack of cavitation in the homogeneous supercritical phase provides the advantages of increased thermal efficiency and simpler design. Before such technologies can be developed, an understanding of the complex properties of water and aqueous solutions in the near and supercritical region must be understood. For example, the solubilities of iron oxide and hydroxide corrosion products as well as the formation rates and transport properties of corrosive oxidizing species such as oxygen, are required in order to develop adequate corrosion control chemistry for the SCWR.<sup>15–20</sup> However the experimental difficulties of obtaining data at these temperatures and pressures have traditionally imposed limitations on what can be ascertained regarding the behavior of water at these extreme conditions.

From a chemical perspective, the diffusion coefficients of water and reactive species are needed for an estimation of the diffusion-controlled limit of reaction rates. Svishchev and Plugatyr used a flow-through reactor along with molecular dynamics simulations to study the degradation of dichlorobenzene in water and to determine the diffusion-controlled limit of the reaction rates of a hydroxyl radical and phenol in supercritical water.<sup>21</sup> They have performed classical simulations of a hydroxyl radical in water at near and above the critical point, to provide data on the kinetics of oxidation reactions.<sup>22</sup> O<sub>2</sub>, H<sub>2</sub>, and OH radicals are the radiolysis products of water in

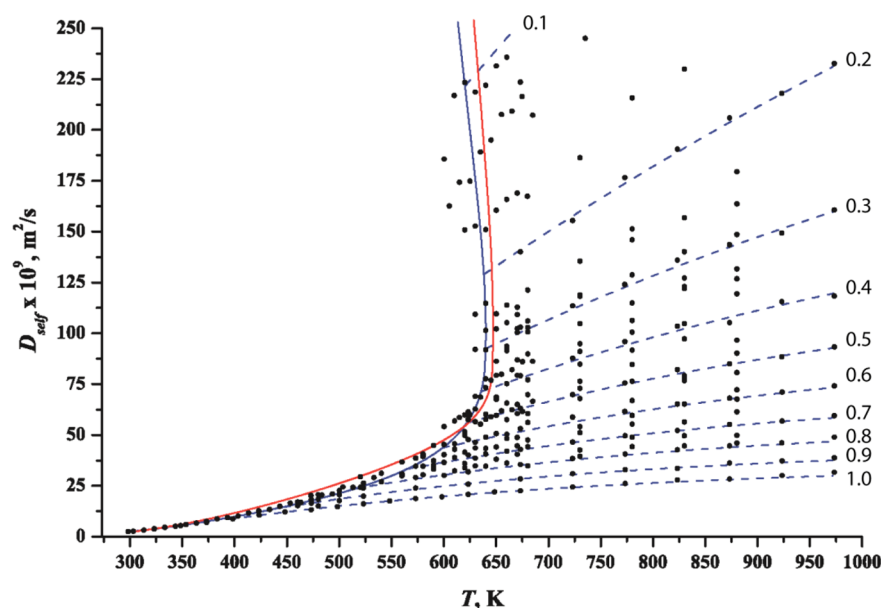
the in-core components of the SCWR.<sup>23,24</sup> O<sub>2</sub> and OH radicals are highly aggressive in terms of their corrosiveness to the water-bearing components in the SCWR, and they react with chemical additives, thus their behavior in supercritical water is of significant importance. Any H<sub>2</sub> gas evolved in the system may have a role in scavenging these species, thereby inhibiting oxidation in the reactor piping. Ghandi and Percival used a radiolysis model for muonium kinetics and reached a conclusion that the rate constant for a OH radical with a hydrated electron in water has non-Arrhenius behavior at high temperature conditions.<sup>25</sup> Codorniu-Hernandez and Kusalik used ab initio molecular dynamics to examine OH hydration structure.<sup>26</sup> A classical molecular dynamics study in 2012 by Swiatla-Wojcik and Szala-Bilnik provided a detailed analysis of the hydration, pair distribution functions, and interaction energies of a hydroxyl radical in water,<sup>27</sup> with the results being similar to those obtained by Svishchev and Plugatyr. In this work we utilize a classical model for OH, as it is computationally tractable, and the results of previous studies<sup>27,28</sup> using classical models of OH derived from ab initio force fields to generally give a similar picture of hydration at high temperature as ab initio calculations.

In the past it was believed that the thermal energies of the water molecules in the supercritical regime were too great to allow much hydrogen bonding. More recently the pair correlation functions from neutron diffraction, IR spectroscopy, and molecular dynamics simulations, suggest that there is in fact some degree of limited hydrogen bonding present in the system.<sup>29–36</sup> Although supercritical water loses most of the preferred tetrahedral network structure that is seen at ambient conditions, hydrogen-bonded complexes can be observed. These short-lived configurations form and break apart on a

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**Figure 1.** Temperature dependence of the self-diffusion coefficients of SPC/E water. Blue dashed lines represent isochores from 0.1 (top) to 1.0 g cm<sup>-3</sup> (bottom) and correspond to the self-diffusion coefficients obtained from eq 1 for SPC/E water. Black dots represent the self-diffusion coefficients from our MD simulations. Blue and red solid lines show the coexistence curve calculated from our EOS for SPC/E water and Yoshida's experimental data, respectively.

time scale similar to that of the lifetime of a hydrogen bond, roughly on the order of tens of picoseconds. Despite the presence of these water–water associates, the extent of the breakdown of tetrahedral structure in supercritical water is enough to allow more mobility for the molecules and hence an increase in the self-diffusion coefficients as temperature increases with a corresponding drop in density.

Viewed from the atomistic perspective, molecular dynamics simulations have now become a viable and time effective method for providing detailed information of the reaction dynamics of water and solvated species at high temperature and supercritical conditions. The simple point charge (SPC/E) model of water has been found to accurately reproduce physical and thermodynamic properties, including dielectric constant and self-diffusion coefficient, over a wide range of temperatures and pressures.<sup>37,38</sup> The SPC/E model provides through the principle of corresponding states, accurate thermodynamic behavior of water, particularly at high temperatures and in the supercritical region.<sup>39,50</sup>

In this study, the SPC/E model was used to perform classical molecular dynamics simulations of pure water as well as infinitely dilute aqueous solutions of O<sub>2</sub>, H<sub>2</sub>, and an OH radical species, in the supercritical region, as well as along the liquid branch of the liquid–vapor coexistence line. The transport properties of pure water and these infinitely dilute species were calculated using the density expansion of the correlation function expression for the diffusion coefficients of three-dimensional gases, based on a hard sphere collision model, as formulated by Kawaski and Oppenheim.<sup>40</sup> Their formulation of the diffusion coefficient is

$$D\rho = aT^\alpha + \rho(b_1T^{-2} + b_2T^{-1} + b_3 + b_4T) + \rho^2\ln\rho(c_1T^{-2} + c_2T^{-1} + c_3 + c_4T) + \rho^2(d_1T^{-2} + d_2T^{-1} + d_3 + d_4T) \quad (1)$$

where  $a$ ,  $\alpha$ , and  $b$ ,  $c$ ,  $d$  are the fitting parameters,  $T$  is temperature in Kelvins, and  $\rho$  is the water density, in g cm<sup>-3</sup>.

Over 370 state points were simulated for pure water and over 30 for each infinitely dilute species. Equation 1 was fitted to the simulation data. The results for the self-diffusion coefficients of water obtained by our method were compared against the NMR experimental diffusion data obtained by Yoshida et al.<sup>41</sup> The results of our study show that the SPC/E model with our parametrization of Kawaski's equation gives results within 6 % of experiment for water, the statistical uncertainty of the simulated transport coefficients for water also being around 5 %. Because of the lack of data for H<sub>2</sub>, O<sub>2</sub>, and OH radical in the broad range of state conditions, the diffusion coefficients for these species extrapolated from our high-temperature model fits were compared to simulated and experimental values at ambient conditions, in order to validate their accuracy and viability for extrapolation.

## 2. COMPUTATIONAL METHODS

The transport properties of the SPC/E water model were obtained in the NVT ensemble by using classical Lagrangian based molecular dynamics. Over 370 simulations were performed for water and 30 for each infinitely dilute O<sub>2</sub>, H<sub>2</sub>, and OH radical system. A detailed description of our selection of state points for the SPC/E water and its thermodynamics can be found in ref 50. The simulated systems ranged in temperatures from 298 K to 973 K and densities from 0.1 to 1.0 g cm<sup>-3</sup> and consisted of 343 water molecules and one molecule of the respective species investigated. A cubic simulation cell was used along with periodic boundary conditions to simulate an infinite system. The fourth order Gear algorithm<sup>42</sup> was used to obtain the equations of motion with a time step of 1 fs, and output was recorded every 1000 steps. Rotational degrees of freedom were represented by quaternions.<sup>43</sup> The potential used for SPC/E water used was taken from Berendsen et al.<sup>44</sup> The potential for the OH was taken from Wiener et al.,<sup>45</sup> as modified by Svishchev and Plugatyr,<sup>22</sup> and those for O<sub>2</sub> and H<sub>2</sub>

are taken from Hansen,<sup>46</sup> and Cracknell,<sup>47</sup> respectively. Ewald summation was used to evaluate the long-range Coulombic interactions, and the Lorentz–Berthelot mixing rules were used to create Lennard-Jones atomic potentials.<sup>48</sup> Simulations were run for 3 ns to allow sufficient convergence of the velocity autocorrelation functions for the calculation of the diffusion coefficients. The statistical uncertainty in the diffusion coefficients was found to be within 15 % for O<sub>2</sub>, H<sub>2</sub>, and OH, and within 5 % for H<sub>2</sub>O. Simulations were performed on the Shared Hierarchy Academic Resource Computing Network (SHARCNET) which is operated by a consortium of Ontario Universities.

### 3. RESULT AND DISCUSSION

The diffusion coefficients for pure SPC/E water are shown explicitly in Figure 1. Equation 1 was fitted to the data using a nonlinear regression over all simulated high-temperature state points (above 460 K), the variables being temperature and density. It was found that an accurate fit for our formulation of Kawaski's expansion could be obtained with 14 coefficients. For water and each species O<sub>2</sub>, H<sub>2</sub>, and OH radical, a unique set of fitting parameters was obtained. The fitting parameters are given in Table 1. The mean relative error of the fit was

**Table 1. Fitting Parameters of Equation 1 for the Diffusion Coefficients for Water, OH Radical, H<sub>2</sub>, and O<sub>2</sub><sup>a</sup>**

fit coefficients	H <sub>2</sub> O	OH radical	H <sub>2</sub>	O <sub>2</sub>
<i>a</i>	0.0046471	0.00408	116.211	1.82779
<i>α</i>	1.2939	1.38897	0.0538917	0.422868
<i>b</i> <sub>1</sub>	1.05646·10 <sup>8</sup>	1.0	1.0	1.0
<i>b</i> <sub>2</sub>	−511648	−174613.7394	372312	−102443
<i>b</i> <sub>3</sub>	691.903	847.03131	−1794.21	334.021
<i>b</i> <sub>4</sub>	−0.1729	−0.71041	1.42193	−0.119239
<i>c</i> <sub>1</sub>	8.88978·10 <sup>7</sup>	1.0	1.0	1.0
<i>c</i> <sub>2</sub>	−358381	−153864.1999	476427	−102959
<i>c</i> <sub>3</sub>	334.773	782.41564	−1880.99	334.195
<i>c</i> <sub>4</sub>	0.0213276	−0.64852	1.62233	−0.117517
<i>d</i> <sub>1</sub>	−1.01281·10 <sup>8</sup>	1.0	1.0	1.0
<i>d</i> <sub>2</sub>	475755	163191.6423	−377905	100433
<i>d</i> <sub>3</sub>	−608.627	−795.71944	1654.15	−347.059
<i>d</i> <sub>4</sub>	0.116203	0.63849	−1.39764	0.125558

<sup>a</sup>The mean relative error of the fit of eq 1 to the simulated data is estimated to be less than 1 %.

determined to be on the order of 1 % in the diffusion coefficients which is significantly less than the statistical uncertainty of simulation (approximately 5 % for water, and 15 % for O<sub>2</sub>, H<sub>2</sub>, and OH). Kawaski's density expansion is valid for conditions along the water–vapor coexistence curve as well as in the high temperature and supercritical regimes. The SPC/E water density along the coexistence curve (at high temperatures), and in the supercritical region can be calculated using the thermodynamic equation of state developed by Plugatyr and Svishchev.<sup>38,50</sup> We also point out that although our parametrized eq 1 can accurately predict the SPC/E model diffusion coefficients from ambient conditions upward to 973 K we recommend its technical use be restricted to temperatures ranging from 460 K to 880 K and densities only up to 0.92 g/cm<sup>3</sup>, where the thermodynamic equation of state for SPC/E water accurately predicts the coexistence properties and derivatives of the pressure. For a detailed description of our

SPC/E equation of state, readers are referred to Plugatyr et al.<sup>38,50</sup>

For water, the temperature dependence of the diffusion coefficients can be seen in Figure 1. The diffusion coefficients are plotted as isochores as a function of temperature ranging from ambient to 973 K, with densities ranging from 0.1 to 1.0 g cm<sup>−3</sup>, from top to bottom. The black dots represent the results of our MD simulations and the blue dashed lines represent the diffusion coefficients calculated from eq 1. The coexistence curve data calculated from Yoshida's experimental fit<sup>49</sup> and that from the simulation, using the SPC/E equation of state,<sup>50</sup> are shown in red and blue solid lines, respectively. It can be seen that our fits for SPC/E water closely follow the coexistence curve data produced for real water, as formulated by Yoshida et al. Also evident from the figure is the close match of our simulated diffusion coefficients to those of our parametrization along each isochore.

Using our fitted equation, diffusion coefficients were calculated and compared to the experimental NMR results of Yoshida, for state points both along the liquid side of the coexistence curve, as well as in the supercritical region. Our values were tested against Yoshida's results in 50 K intervals from 303.15 K to 673.15 K.<sup>41</sup> Using our set of coefficients for water, the calculated diffusion coefficients accurately matched Yoshida's experimental values to within an average of 5.8 %. At 303.15 K we obtained a value of  $(2.74 \pm 0.14) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , compared to Yoshida's measurement of  $(2.61 \pm 0.05) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . For the supercritical conditions of 623.15 K and density of 0.251 g cm<sup>−3</sup>, our result was  $(132.6 \pm 6.6) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , compared to Yoshida's value of  $(125 \pm 6) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ .

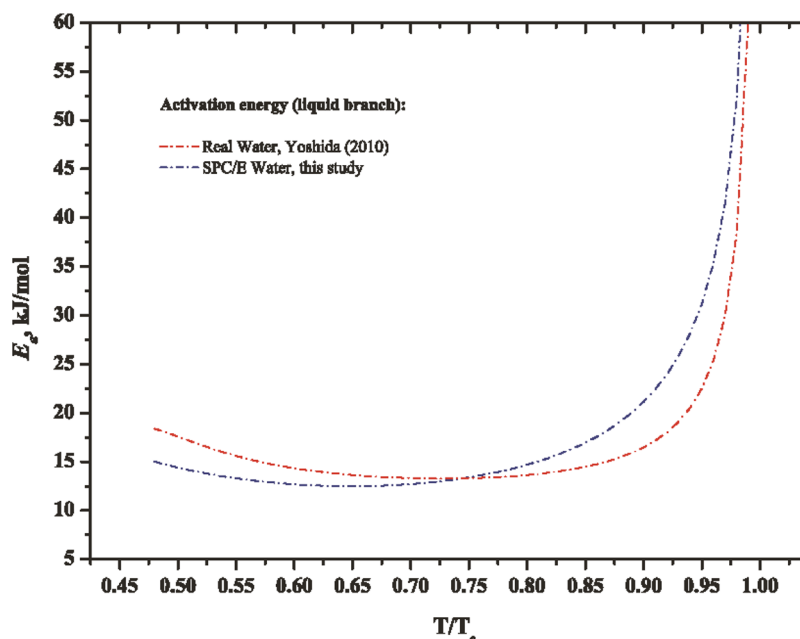
Due to the lack of experimental data for O<sub>2</sub>, H<sub>2</sub> and OH radicals in the broad range of state conditions, the diffusion coefficients extrapolated from our high temperature fits were compared to the results from our MD simulations at ambient conditions of 298 K and 1.0 g cm<sup>−3</sup>. Our parametrization predicts the values  $(2.56 \pm 0.12) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for O<sub>2</sub>,  $(6.37 \pm 0.32) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for H<sub>2</sub>, and  $(2.71 \pm 0.14) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for the OH radical, in SPC/E water solvent. Our explicit MD results were  $(2.81 \pm 0.42) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $(5.22 \pm 0.78) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , and  $(3.46 \pm 0.52) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for O<sub>2</sub>, H<sub>2</sub>, and the OH radical, respectively. This yields 9 % extrapolation error for O<sub>2</sub> and 22 % for both H<sub>2</sub> and OH radical.

Bartels and Han used the Taylor dispersion method to determine the diffusion coefficients for O<sub>2</sub> from 273 K to 368 K.<sup>51</sup> They reported a measured diffusion coefficient of  $(1.960 \pm 0.063) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for ambient conditions, and a value of  $(6.800 \pm 0.052) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 368.15 K. These experimental values are in 82 % agreement with our model predictions for 298.15 K, as obtained from eq 1, and are in 95 % agreement at 368.15 K.

Further validation of our parametrization comes from simulations of O<sub>2</sub> in supercritical water by Ohmori and Kimura.<sup>52</sup> In their simulations using an SPC/E water model, Ohmori and Kimura obtained diffusion coefficients of  $(40 \pm 2) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at a temperature of 647 K, and density of 0.663 g cm<sup>−3</sup>, and a coefficient of  $(189 \pm 12) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 873 K and 0.217 g cm<sup>−3</sup>. These are essentially identical with the values from our parametrization of  $(41 \pm 2) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $(196.0 \pm 9) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ .

The activation energy of our polynomial equation was plotted for temperatures along the coexistence line with an Arrhenius type equation:





**Figure 2.** Activation energy for the self-diffusion of water as a function of reduced temperature. Our calculated values for SPC/E water are shown in blue, and Yoshida's experimental data for real water are shown in red.

$$E_a = -R \left( \frac{\partial \ln D}{\partial \left( \frac{1}{T} \right)} \right) \quad (2)$$

The activation energy and diffusion coefficients from our parametrization for SPC/E water along with Yoshida's results are shown in Figure 2, for reduced temperatures of 0.45 to 1.0. It is in this temperature range that our thermodynamic equation of state formulated for SPC/E water is most accurate. In Figure 2, our results for the activation energies for the self-diffusion of SPC/E water are shown in blue, and the experimental values of Yoshida for real water are shown in red. The activation energy shows a slight rise at the lower end of the temperature scale which can be attributed to the necessity of overcoming the attractive forces imposed by the hydrogen bonds of the water. These forces tend to decrease as temperature increases owing to the thermal energy of the molecules as sufficient to overcome the attraction with their neighboring molecules. Near the critical temperature, a sharp rise is seen in the activation energy which Yoshida has attributed to the increase in the density fluctuations with temperature as one nears the critical temperature.<sup>41</sup>

#### 4. CONCLUSIONS

The logarithmic polynomial density expansion of Kawasaki's equation for hard sphere collisions is shown to be viable for SPC/E water and accurately reproduces experimental diffusivity data along the liquid branch of the coexistence line as well as in the high temperature region, including the supercritical phase. For pure water and for each infinitely dilute species, O<sub>2</sub>, H<sub>2</sub>, and the OH radical, a unique set of 14 coefficients have been provided and have been found sufficient to accurately obtain the diffusion coefficients, with the only system variables being temperature and density. Our simulation-based formulation for pure water closely reproduces the experimental data obtained by Yoshida along the vapor–liquid coexistence line as well as the activation energy. The formulations developed are

recommended for use between 460 K and 880 K where the thermodynamic equation of state for SPC/E water most accurately reproduces physical properties. They provide a fast, simple, and accurate method by which to calculate mass transport coefficients in high temperature aqueous solutions, for general and engineering use. Additional simulations of H<sub>2</sub>O<sub>2</sub> and other radiolytic species produced in the reactor would be beneficial to extend our parametrization database.

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##### Notes

The authors declare no competing financial interest.

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