Radiation chemistry in SCWR

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Abstract

In 2002, Ghandi and co-workers proposed a model that includes an efficiency factor to account for the "cage effect". This model reproduces the plateau observed in available experimental data. Our group is working on reviewing all the reactions considered in the report submitted by Atomic Energy of Canada Limited in 2009 based on the cage effect model, in order to provide recommendations for the values of rate constants to use in modeling of water radiolysis reactions past the critical point. In this paper, we will be focusing on the very fast reactions that are diffusion controlled past the critical point.

1. Introduction

Nuclear energy is very important for world these days. In 2009, there have been close to 440 operating nuclear power reactors world-wide [1]. Nuclear power has made up 7% of the world's total energy production, and 14.7% of its electricity production [2]. It is estimated that the currently operating nuclear reactors avoid the emission of approximately two billion tons of greenhouse gas each year [3].

The world has seen many generations of nuclear reactors [3], namely generation I, II, III, III+. Each generation has improvements in some aspects. The next generation of nuclear reactors that are currently under development are the generation four (GenIV). The Canadian GenIV design is a supercritical water cooled reactor (SCWR) which uses supercritical water (SCW) as its coolant. SCW is water under high pressure and temperature (above 374 °C, 22.1 MPa). By increasing the temperature and pressure of the water, SCWR can achieve a thermal efficiency of 44% compared to the current generation light water reactors with efficiencies of ~ 33% [4]. One of the difficulties for SCWR development is the lack of knowledge concerning the reaction kinetics in SCW. Most of the reactions in water react significantly faster as temperature increases to ~ 300 °C [5]. Some of the by-products generated by these reactions can build up with time, and can potentially damage the reactor core. It is essential to understand these reactions in order to build a safe and economic SCWR.

Various studies have shown the rate constants for different reactions in water go through a plateau before reaching the critical point [6–12]. Based on those studies, published models using Noyes' equation which relies on Arrhenius behaviour of rate constants can seriously overestimate the rate constants for many reactions at high temperatures. Modeling radiolysis and water chemistry for supercritical water cooled reactor technology however requires accurate predictions for rate constants past the critical point. Our group has been working on a model called cage effect model that includes an efficiency factor to account for the "cage effect". We are attempting to model all the reactions that were studied in a report submitted by Atomic Energy of Canada Limited in 2009 (AECL report) [5]. Most of the reactions we modeled are activation-controlled past the critical point due to the cage effect. For some very fast reactions however, we found they are still diffusion-controlled after the critical point. In this paper, we will be focusing on these very fast reactions, and give a short review of diffusion rate constant at high temperature in water. The detailed methodology was described in another paper [8].

2. Methodology

In the Noyes equation (1), the observed reaction rate constant k_{obs} [13] is expressed as:

$$\frac{1}{k_{obs}} = \frac{1}{k_{diff}} + \frac{1}{k_{react}} \quad (1)$$

k_{diff} is the diffusion rate constant, and k_{react} is the chemical reaction rate constant.

k_{diff} is usually calculated using the Stokes-Einstein equation (SEE). Most of the constants in SEE are temperature independent; when we calculate k_{diff}, we combine these constants into one constant $B(\text{r})$, so calculation of k_{diff} becomes:

$$k_{\text{diff}} = B(\text{r}) \text{ x } \frac{T}{\eta} \quad (2)$$

B(r) is a fit parameter, T is the temperature, and η is viscosity. k_{react} usually has an Arrhenius temperature dependence; our calculations include an additional factor f_{R} to account for the cage effect:

$$k_{\mathrm{react}} = f_{\mathrm{R}}\, A\, \mathrm{e}^{\frac{-Ea}{RT}} \quad (3)$$

A is the pre-exponential factor, Ea is the activation energy, and R is the universal gas constant.

f_{R} represents an efficiency factor of collisions per encounter, and has the form (4):

$$f_{\mathrm{R}} = \frac{p_{\mathrm{R}} k_{\mathrm{gas}} \times (\frac{\eta}{T})}{k_{diff} + p_{\mathrm{R}} k_{\mathrm{gas}} \times (\frac{\eta}{T})} \quad (4)$$

In the above equation, $p_{\mathrm{R}}k_{\mathrm{gas}}$ is the rate of potentially reactive collisions and k_{diff} is the rate of encounters (calculated in (2)). $p_{\mathrm{R}}k_{\mathrm{gas}}$ is proportional to solvent viscosity, and inversely proportional to the temperature, and is therefore proportional to $(\frac{\eta}{T})$ [8], [12], [14].

The pre-exponential factor A, activation energy Ea, rate of potentially reactive collisions $p_{\mathrm{R}}k_{\mathrm{gas}}$ (the constant multiplied by viscosity/ temperature) and the constant B(R) are all assumed to be temperature independent fitting parameters in this work, and are used in fitting experimental data.

3. Results and Discussion

Although the k_{diff} used in our model works very well with experimental data at low temperature (below 300 $^{\mathrm{o}}$C), there are very little experimental data to test our model at higher temperatures. In 2005, Svishchev *et al.* [15] studied the temperature dependence of diffusion coefficients of water and OH using molecular dynamics (MD) simulations. In the same year, Yoshida *et al.* [16] studied diffusion coefficient up to 400 °C using nuclear magnetic resonance (NMR) experiment and MD simulation. Using Yoshida's experimental data, Kallikragas *et al.* [17] fitted the diffusion coefficient of water, and OH radical, up to 607 °C. The data point mentioned are shown in Figure 1, based on Yoshida's experimental data, Kallikragas's fit would predict a higher diffusion coefficient than we would have predicted past critical point.

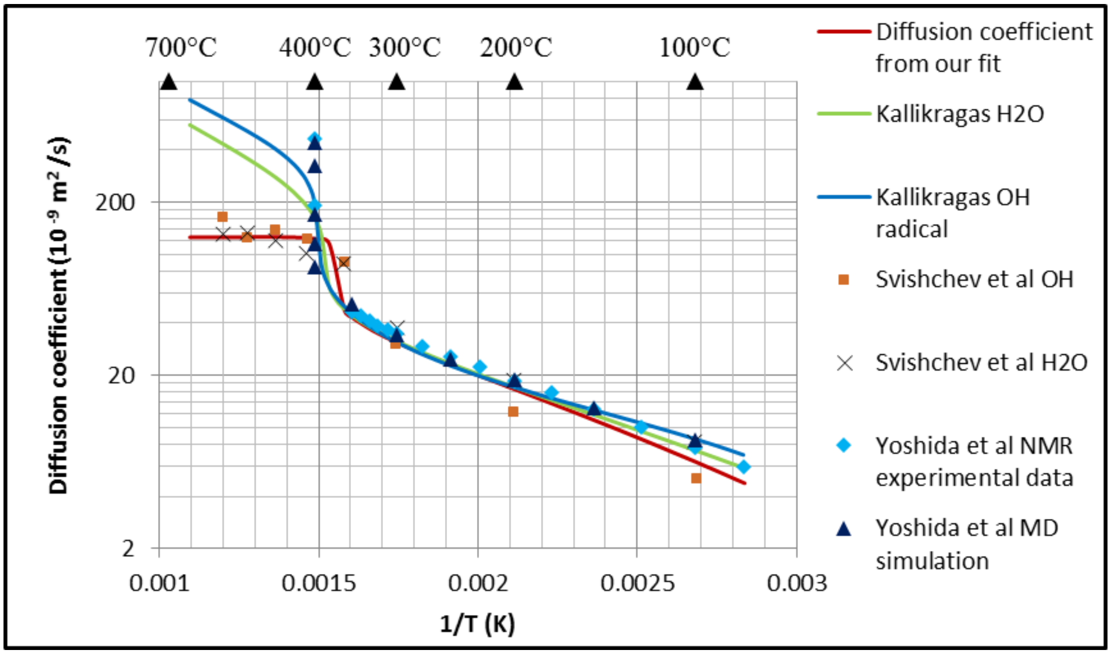

Figure 1 Diffusion coefficient from different works: Yoshida *et al.* MD simulation (triangles), NMR experiment (diamonds), Svishchev *et al.* MD simulation OH (squares), H_2O (cross), lines order from bottom, scaled k_{diff} from our fit (red), Kallikragas's H_2O (green), OH (blue).

This difference in k_{diff} won't significantly influence our fits for most reactions, because our model predict an activation controlled reaction past critical point for most of the reactions due to the significant drop of chemical reaction rate constants. This can be demonstrated using Figure 2, the graph in the top is a fitted experimental data of reaction: $e_{aq}^{-} + \cdot OH \rightarrow OH^{-}$ produced using our model. We replace the diffusion coefficient in the same graph with a scaled diffusion coefficient of water from Kallikragas's fitting shown in the bottom. One can see that the difference between the diffusion coefficients at high temperature range does not significantly change the k_{obs}.

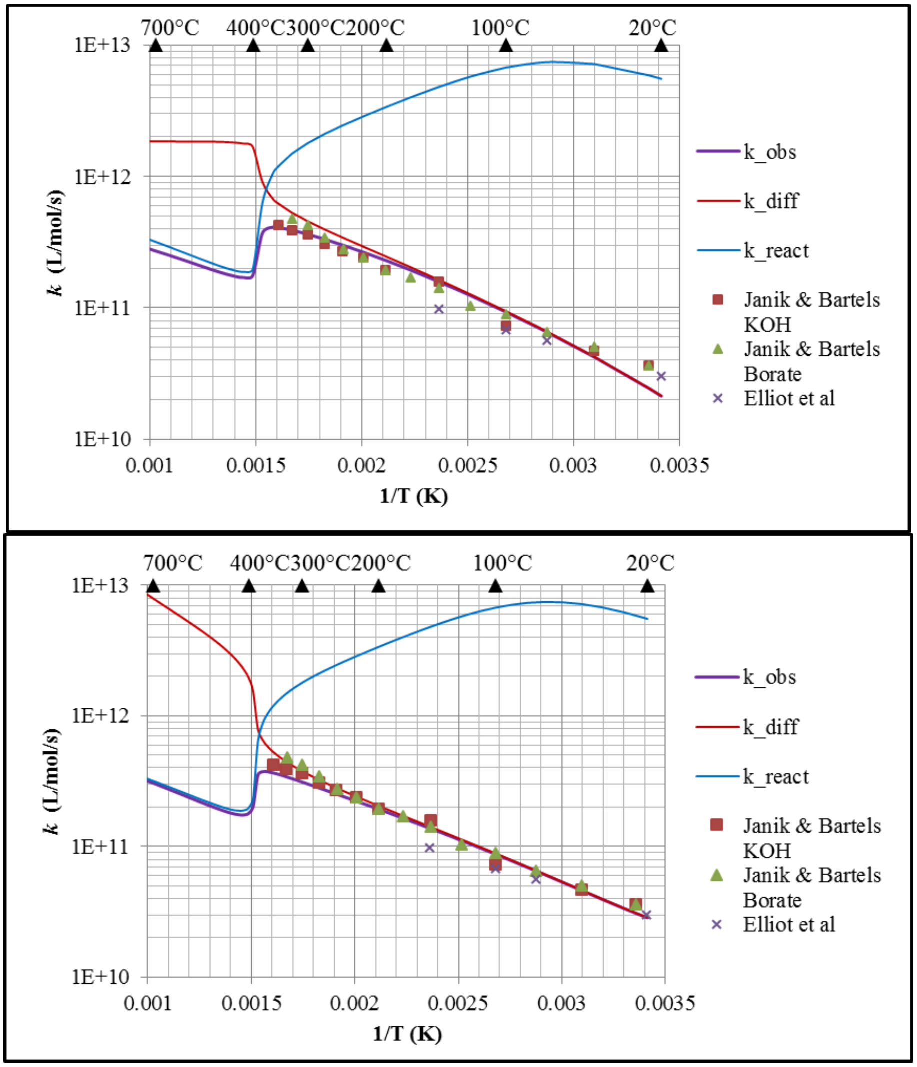

Figure 2 (top) fitted k_{react} (3), k_{diff} (2) and k_{obs} (1) of reaction: e_{aq}^{-} + $\cdot OH \rightarrow OH^{-}$. (bottom) the same graph but the diffusion coefficient is replaced by a scaled diffusion coefficient of water from Kallikragas's fit. Experimental data are from Janik and Bartels [5] (red) (green), Elliot *et al.* (cross) [18].

However for the reaction: $H^+ + e_{aq}^- \rightleftharpoons H\cdot$, our model predicts a diffusion controlled reaction even past critical point (Figure 3). For this reaction a modification is necessary to the k_{diff}. One can see the modified fit (bottom) is much better.

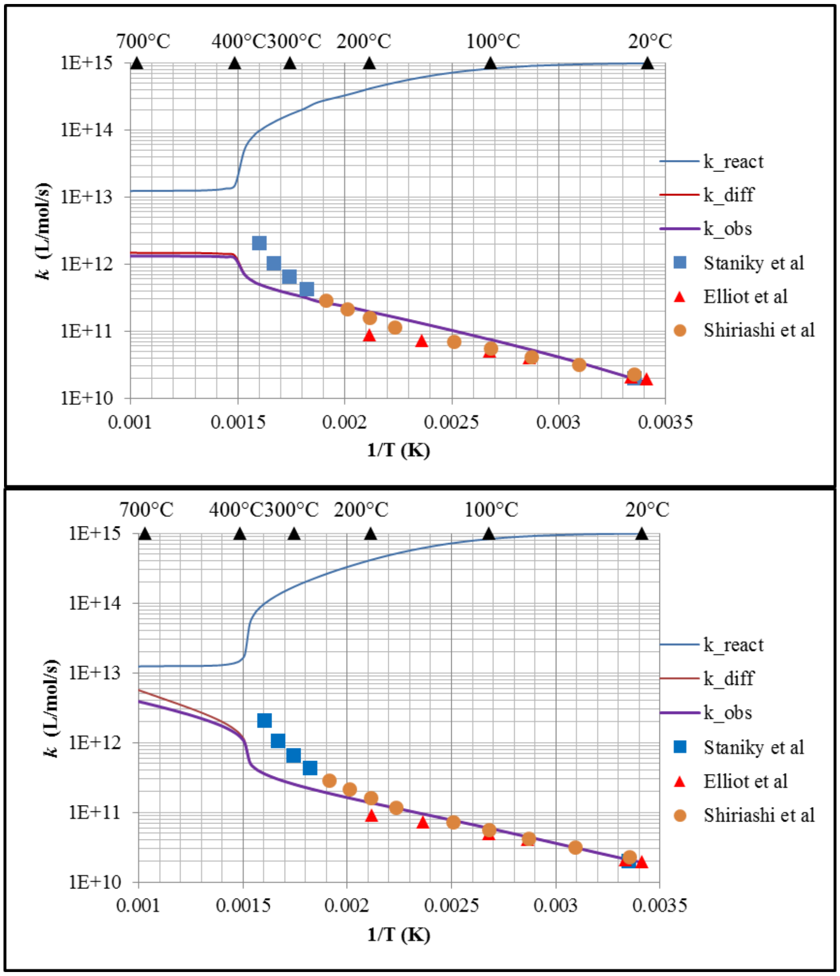

Figure 3 (top) fitted k_{react} (3), k_{diff} (2) and k_{obs} (1) of reaction: $H\cdot \rightleftharpoons H^+ + e_{aq}^-$. From the figure, one can see that the reaction is still diffusion controlled past critical point. (bottom) our fit with a modified k_{diff}. A scaled k_{diff} of water based on the diffusion coefficients from the work of Kallikragas *et al.* [17] is used as the k_{diff} here. Experimental data are from Bartels, Elliot *et al.* (triangles) [19], Stanisky *et al.* (squares) [20] and Shiraishi *et al.* (circles) [21].

$H^+ + e_{aq}^- \rightleftharpoons H\cdot$ is a very interesting reaction that involves opposite charged reactants. The special thing about this reaction is that the rate of reaction increases significantly after 230 °C, this dramatic change has been confirmed in multiple sources [20]. This sudden increase of rate constant can be caused by the change of dielectric constant of the solvent water. Dielectric constant, which describes how well a medium can support ions, decreases as temperature increases in water [22]. Our model does not take into account of the effect of dielectric constant directly; charged reactants however can be influenced by the electric field of water when they react. For other reactions that do not involve opposite charged reactants, we do not see this sudden increase of rate constant (although a sudden increase is seen for the reaction: $O_2^- + HO_2\ (+H_2O) \rightarrow H_2O_2 + O_2 + OH^-$; the rate constant is recommended to be re-investigated with knowledge of the decay rate of HO_2/O_2^- as a function of pH and pK_A of HO_2 and extinction coefficient of O_2^- and HO_2 [5]).

It is suggested that the yield of H atoms and electrons should be nearly equal in water vapour, however this ratio is strongly in favor H atoms in supercritical water [5], [7], [23]. Although, there are many reactions that remove H atoms, there are only a few reactions that produce H atoms in radiolysis ($H^+ + e_{aq}^- \rightleftharpoons H\cdot$ and $H_2 + \cdot OH \rightleftharpoons H\cdot + H_2O$). In order for the yield of H to increase, there has to be a channel that produces H atoms. A sudden increase of the rate constant of $H^+ + e_{aq}^- \rightleftharpoons H\cdot$ reaction can be the cause of the increase of the H atoms yield.

There are not much data for reactions involving opposite charged reactants in water. In fact, $H^+ + e_{aq}^- \rightleftharpoons H\cdot$ is the only reaction with experimental data at high temperature. There are other reactions in water that involve opposite charged reactants, for example:

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$H^+ + HO_2^- \rightleftharpoons H_2O_2$$

$$H^+ + O^- \rightleftharpoons \cdot OH$$

$$H^+ + O_2^- \rightleftharpoons HO_2$$

Based on our model, we believe all of these reactions would be almost three orders of magnitudes faster at the maximum SCWR temperature compared to their room temperature values. Therefore we suggest measuring those reactions either by pulse radiolysis or muon methods.

4. Conclusion

It is essential to understand the reactions in SCW in order to build safe and economic SCWRs. In this paper, we discussed the k_{diff} from different works, and how a modified k_{diff} would influence the predicted data on rate constants. The reactions that involve opposite charges need to be paid much attention to and needs to be measured by experimental techniques such as pulse radiolysis and muon methods. Our fits suggest those reactions can be diffusion controlled reactions past critical point, and are fastest in the range that SCWRs operating on (around 650°C).

5. Acknowledgment:

This research was financially supported by the Generation IV Energy Technologies Program of the Natural Sciences and Engineering Research Council of Canada, Natural Resources Canada and Atomic Energy of Canada Limited. Computational work was performed on the Atlantic Computational Excellence Network (ACENet).

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