

On the Temperature Dependence of the Rate Constant of the Bimolecular Reaction of two Hydrated Electrons

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ABSTRACT

It has been a longstanding issue in the radiation chemistry of water that, even though H₂ is a molecular product, its “escape” yield $g(\text{H}_2)$ increases with increasing temperature. A main source of H₂ is the bimolecular reaction of two hydrated electrons (e_{aq}^-). The temperature dependence of the rate constant of this reaction (k_1), measured under *alkaline* conditions, reveals that the rate constant drops abruptly above ~150°C. Recently, it has been suggested that this temperature dependence should be regarded as being independent of pH and used in high-temperature modeling of *near-neutral* water radiolysis. However, when this drop in the e_{aq}^- self-reaction rate constant is included in low (isolated spurs) and high (cylindrical tracks) linear energy transfer (LET) modeling calculations, $g(\text{H}_2)$ shows a marked downward discontinuity at ~150°C which is *not* observed experimentally. The consequences of the presence of this discontinuity in $g(\text{H}_2)$ for both low and high LET radiation are briefly discussed in this communication. It is concluded that the applicability of the sudden drop in k_1 observed at ~150°C in alkaline water to near-neutral water is questionable and that further measurements of the rate constant in pure water are highly desirable.

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INTRODUCTION

In nuclear power plants (NPPs), water is used as both a coolant and neutron moderator. Over the operating temperature range of 275-325°C, water is irradiated heavily in the reactor core by some mixture of fast electrons and recoil ions of hydrogen and oxygen, which have characteristically different linear energy transfer (LET) values (in the range from ~0.3 to 40-60 keV/μm, respectively). This irradiation results in the chemical decomposition (radiolysis) of water and leads to the formation of the short-lived reactive radicals e_{aq}^- (hydrated electron), H[•], •OH, and HO₂• (or O₂•⁻, depending on pH) and the longer-lived molecular products H₂ and H₂O₂ (and eventually O₂). These species can promote corrosion, cracking, and hydrogen pickup both in

the core and in the associated piping components of the reactor [1-5].

Theoretical calculations and chemical models of the radiation chemistry of water in the reactor core require the radiolytic yields (defined as the number of species formed or destroyed per 100 eV of energy absorbed [6,7]) of the primary species for both fast neutrons and γ-radiation. The rate constants for *all* of the reactions involving these species are also required. The yields and chemical kinetic data for high-temperature light water radiolysis, up to 350°C, have recently been compiled and reviewed by Elliot and Bartels [8].

For water at neutral or near-neutral pH under low-LET radiation (such as ⁶⁰Co γ-rays and fast electrons), the *primary* (or “escape”) yields (commonly denoted g -values) of the free radicals e_{aq}^- , H[•], and •OH continuously increase when the temperature is increased, while the primary yield of H₂O₂ decreases [8,9]. Although H₂ is a molecular product, $g(\text{H}_2)$ increases monotonically with

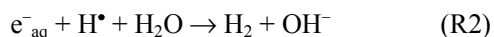
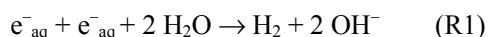
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temperature, particularly above 200°C [8-13]. H₂, whose formation is favored by fast neutron (high-LET recoil-ion) radiolysis [4], is an important component associated with the corrosion environment of the coolant system in NPPs. Knowledge of the production of H₂ from irradiated water and the amount of “excess” H₂ to be added to the primary coolant to mitigate water decomposition and O₂ production is crucial to develop better reactor chemistry control and to optimize plant performance [14-16].

THEORY

In the γ -radiolysis of water, there are several different mechanisms for the production of molecular hydrogen. Recent studies have shown that a major fraction of the total H₂ formed [$g(\text{H}_2) = 0.45$ molecule/100 eV at 25°C (for conversion into SI units, 1 molecule per 100 eV $\approx 0.10364 \mu\text{mol J}^{-1}$)] is due to reactions involving the precursors of the hydrated electron at short (< 1 ps) times after the initial passage of the radiation [17,18]. These reactions include the dissociation of excited water molecules formed by recombination of the nonhydrated electron with its parent cation H₂O⁺ (geminate recombination) and the dissociative attachment of subexcitation-energy electrons (those that have kinetic energies lower than the first-electronic excitation threshold of the medium, i.e., ~ 7.3 eV in liquid water) to a water molecule (DEA) [19]. Most of the rest of the formation of H₂ is due to the following combination reactions between e⁻_{aq} and H[•] atoms during spur/track expansion (typically, on time scales from ~ 1 ps to 1 μs) [6-8,10]:



and (above $\sim 200^\circ\text{C}$) [9,15,20-22]



The new self-consistent radiolysis database of Elliot and Bartels [8] provides recommendations for the best values to use to model water radiolysis at temperatures up to 350°C. Of particular significance, the rate constant for the self-reaction of e⁻_{aq} (R1) (k_1), measured in *alkaline* water [23-27], exhibits a “catastrophic” drop between 150 and 200°C and, above 250°C, is too small to be measured reliably [8,27]. The mechanism behind this non-Arrhenius behavior above 150°C is not well understood, but it is generally thought to involve the formation of some transient

intermediate, such as a hydrated electron dimer (or “dielectron”, e₂²⁻_{aq}) sharing the same solvent cavity, a hydride ion (H⁻), or yet an “incompletely relaxed” localized electron (e⁻_{ir}) [23,27-29]. The applicability of this drop in k_1 above 150°C to *neutral* solution, however, has long been a subject of discussion because it could be a function of the pH of the solution [24]. For example, in a report published in 2002, Stuart *et al.* [26] wrote, “It still needs to be established whether there is a turnover of the rate constant in neutral solution”. In fact, up to now, most computer modelers of the radiolysis of water at high temperatures have employed, in neutral solution, an Arrhenius extrapolation previously proposed by Elliot [24] and Stuart *et al.* [26]. This approach assumes that such an abrupt change in k_1 does *not* occur and that reaction (R1) is diffusion controlled at temperatures greater than 150°C. This assumption was justified by the good agreement obtained between models and experiment [30-33].

However, in recent reports (and personal communication), Bartels and coworkers [8,27] emphasized that the measured temperature dependence of the (R1) reaction rate constant in alkaline solution should, in fact, be regarded as *independent* of pH and thus used in high-temperature modeling of near-neutral water radiolysis. As predicted earlier, including the drop in k_1 above 150°C in deterministic diffusion-kinetic modeling calculations [30,31,34] and in Monte Carlo simulations [9,32,33] resulted in a sharp downward discontinuity in $g(\text{H}_2)$, which is *not* observed experimentally. Figure 1 illustrates the simulation results of $g(\text{H}_2)$ as a function of temperature as obtained recently by our group at the Université de Sherbrooke [9]. Indeed, above $\sim 150^\circ\text{C}$ the calculations predict a decrease in $g(\text{H}_2)$ instead of the observed increase.

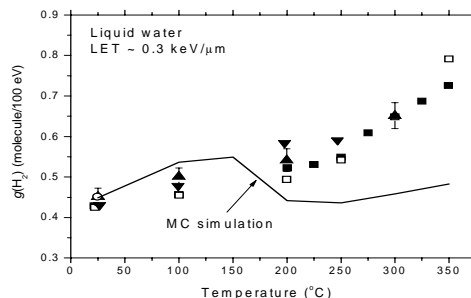


Fig. 1. Temperature dependence of the *primary* yield of H₂ in the low-LET radiolysis of water. The solid line shows the values of $g(\text{H}_2)$ obtained from our Monte Carlo simulations when the drop in the rate constant for the self-reaction of e⁻_{aq} above 150°C is included in the calculations [9]. The predicted $g(\text{H}_2)$ shows a marked inflection around 150-200°C, which is *not* observed experimentally. Symbols are experimental data [6,8,10,11,12].

RESULTS AND DISCUSSION

To obtain acceptable fits of our calculated values of $g(\text{H}_2)$ to the experimental data above 150°C , we had to adjust the temperature dependence of certain parameters involved in the early ($<10^{-12}$ s) “physicochemical stage” [35] of radiolysis, *i.e.*, the thermalization distance of subexcitation-energy electrons (r_{th}), the DEA [19,36,37], and the branching ratios of the different excited water molecule decay channels [9]. Interestingly, $g(\text{H}_2)$ was found to be the yield most sensitive to r_{th} . In fact, to compensate for the decrease of k_1 , a sharp decrease of r_{th} above ~ 100 - 150°C had to be included in the simulations. This decrease in r_{th} was supposed to be the signature of an increase in the scattering cross sections of subexcitation electrons probably reflecting a rapid deterioration in the degree of structural order of water (due to increased breaking of hydrogen bonds) at these temperatures (these subexcitation electrons are known to be very sensitive to the structural order of the surrounding medium, owing to their non-negligible delocalized character) [9,32]. Despite the lack of clear experimental evidence for such a change in the topology of intermolecular hydrogen bonding in water above 150°C , very good agreement was found under these conditions between simulated and experimental $g(\text{H}_2)$, and the sharp downward discontinuity predicted at 150°C (Fig. 1) no longer appeared (see dotted line in Fig. 2) [9].

Recently, however, in the course of a Monte Carlo simulation study of the radiolysis of water by *fast* (2 MeV) neutrons (which produce high-LET recoil protons and oxygen ions) [38], our calculations showed, somewhat unexpectedly, that $g(\text{H}_2)$ exhibited a downward discontinuity at $\sim 150^\circ\text{C}$ similar to that observed at low LET (Fig. 1). Closer examination revealed that this discontinuity was due, here again, to the abrupt drop in the $(e_{\text{aq}}^- + e_{\text{aq}}^-)$ reaction rate constant above 150°C used in the simulations. Unfortunately, the large amount of scatter in the experimental neutron radiolysis H_2 yield data and also their limited availability could not allow us to determine whether or not the predicted discontinuity at 150°C was confirmed experimentally.

The recurrence of this discontinuity of $g(\text{H}_2)$ at $\sim 150^\circ\text{C}$ in the case of the radiolysis of water by fast neutrons prompted us to further investigate the influence of *high-LET radiation*. To our knowledge, the only experimental work reporting the temperature dependence (up to 180°C) of $g(\text{H}_2)$ for the radiolysis of water at high LET is that of Elliot *et al.* [39] (23-MeV $^2\text{H}^+$ and 157-MeV $^7\text{Li}^{3+}$ ions, with dose-average LETs of ~ 11.9 and

62.3 keV/ μm , respectively [40]). Judging from the results of these authors (see Table 2 of [39]), there is apparently *no* evidence of a discontinuity in $g(\text{H}_2)$ at $\sim 150^\circ\text{C}$ (note that measurements were made at three temperatures only: 25 , 95 , and 180°C for both studied ions) (Fig. 2). However, as for the 2-MeV neutron radiolysis of water and as can clearly be seen from Fig. 2, our simulations of Elliot *et al.*'s experiments (using our IONLYS Monte Carlo simulation code under these particular experimental conditions [41,42]) do reveal the presence of a pronounced discontinuity in $g(\text{H}_2)$ at $\sim 150^\circ\text{C}$ whose magnitude increases as the LET increases.

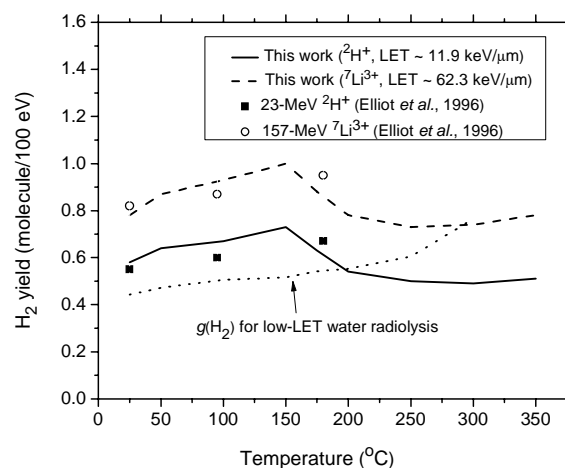


Fig. 2. Variation of the H_2 yield (in molecule/100 eV) of the radiolysis of liquid water by 23-MeV $^2\text{H}^+$ and 157-MeV $^7\text{Li}^{3+}$ ions as a function of temperature over the range 25 - 350°C . Symbols (\circ , \blacksquare) represent the scavenging experimental data of Elliot *et al.* [39] at 25 , 95 , and 180°C , as indicated in the inset. Simulated results (assuming the scavenging power varied linearly from 2×10^7 s $^{-1}$ at 25°C to 6.5×10^7 s $^{-1}$ at 95°C and remaining constant thereafter) are shown as solid (23-MeV deuterons) and dashed (157-MeV $^7\text{Li}^{3+}$) lines. The dotted line shows our simulated primary H_2 yield values for the low-LET (~ 0.3 keV/ μm) radiolysis of water after incorporating a discontinuity around 150°C in r_{th} , DEA, and the branching ratios of the different excited water molecule decay channels [9] [the sharp downward discontinuity predicted for $g(\text{H}_2)$ at 150°C (Fig. 1) no longer appears].

At low LET, we could compensate for the decrease in $g(\text{H}_2)$ predicted by the calculations (instead of the observed increase) by modifying the temperature dependence of r_{th} (and invoking a change in the structure of water at $\sim 150^\circ\text{C}$), whereas at high LET this compensation is, at first sight, no longer straightforward. Briefly, this happens because the number of self-reactions of e_{aq}^- that occur in tracks greatly increases with increasing LET. This means that the influence of the abrupt drop in k_1 , which is at the origin of the $g(\text{H}_2)$ discontinuity, becomes increasingly important as the LET increases. Eventually, it will outweigh the

compensation that was made at low LET, where the number of reactions (R1) in spurs is comparatively much less, thereby allowing the discontinuity of $g(\text{H}_2)$ at 150°C to reappear. A confirmation of these results is offered by the deterministic calculations of Swiatla-Wojcik and Buxton [31] who also modeled Elliot *et al.*'s experiments [39] but without including the drop in k_1 at 150°C; reasonable agreement between the model and experiment was obtained and *no* discontinuity in $g(\text{H}_2)$ at 150°C was observed (see Fig. 1 of [31]).

Under such high-LET conditions, it seems rather difficult, if not impossible, to further modify the temperature dependence of r_{th} (as we did at low LET) in order to counterbalance the effect of the drop in k_1 and obtain acceptable fits of our calculated yields to experimental data. It is, indeed, hardly conceivable that r_{th} would be a function of the LET of the radiation, unless one considers the effects of local temperature increases associated with "thermal spikes" that have sometimes been proposed to occur in the tracks of heavy ions [43-45]).

CONCLUSION

Based on the above findings and in accordance with previous studies [24,26,30-33], we believe that the applicability of the sudden drop in the ($e^-_{\text{aq}} + e^-_{\text{aq}}$) reaction rate constant observed at ~150°C in alkaline water to *neutral* or *slightly acidic* (as the pH of water at 150-200°C is about 5.7-6 [2]) solution, as proposed by Bartels and coworkers [8,27], remain uncertain and should be examined further.

Considering the importance of the self-reaction of e^-_{aq} as a main source of molecular hydrogen in high-temperature water radiolysis, further measurements of its rate constant in pure water are obviously highly desirable. These measurements, which would be extremely beneficial to the modeling community [46], would generate valuable insight for better understanding and predicting reactor coolant water chemistry in NPPs.

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