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ABSTRACT

The yield of molecular hydrogen, as a function of nitric acid concentration, from the α -radiolysis of aerated nitric acid and its mixtures with sulfuric acid containing plutonium or americium has been investigated. Comparison of experimental measurements with predictions of a Monte Carlo radiation track chemistry model shows that, in addition to scavenging of the hydrated electron, its precursor, and the hydrogen atom, the quenching of excited state water is important in controlling the yield of molecular hydrogen. In addition, increases in solution acidity cause a significant change in the track reactions that can be explained as resulting from scavenging of e_{aq}^- by H_{aq}^+ to form H^\bullet . While plutonium has been shown to be an effective scavenger of precursors of molecular hydrogen below 0.1 mol dm^{-3} nitrate, previously reported effects of plutonium on $G(H_2)_\alpha$ between 1 and 10 mol dm^{-3} nitric acid were not reproduced. Modelling results suggest that plutonium is unlikely to effectively compete with nitrate ions in scavenging the precursors of molecular hydrogen at higher nitric acid concentrations and this was confirmed by comparing molecular hydrogen yields from plutonium solutions with those from americium solutions. Finally, comparison between radionuclide, ion accelerator experiments and model predictions leads to the conclusion that the high dose rate of accelerator studies does not significantly affect the measured molecular hydrogen yield. These reactions provide insight into the important processes for liquors common in the reprocessing of spent nuclear fuel and the storage of highly radioactive liquid waste prior to vitrification.

INTRODUCTION

Molecular hydrogen (H_2) production from the radiolysis of aqueous solutions, liquids, and solids is a potential hazard in the nuclear industry because of the possible formation of flammable gas mixtures and pressurisation of sealed containers, such as plutonium (Pu) oxide

canisters. Aqueous nitric acid (HNO₃) solutions are used throughout the nuclear industry for the dissolution of spent nuclear fuel (SNF) and nuclear materials, in SNF reprocessing facilities, and in analytical laboratories. Nitrate anions (NO₃⁻), present in solutions of nitric acid (HNO₃ ⇌ NO₃⁻ + H_{aq}⁺, pK_a ≈ 1.37)¹, are particularly important in the radiolysis of water because they are known to efficiently scavenge the precursors to radiolytic H₂ formation (i.e. the pre-solvated electron (e_{pre}⁻), the hydrated electron (e_{aq}⁻), the hydrogen atom (H[•]), and excited state water (H₂O*)²), to the extent that at high concentrations of nitrate and nitric acid the H₂ yield from water radiolysis is significantly reduced compared with that from pure water.³

There is a large amount of data in the literature for H₂ yields, G(H₂), from the gamma (γ) radiolysis of aqueous nitrate and nitric acid solutions,⁴⁻¹⁴ summarised in Figure 1, due to longstanding interests in the effects of e_{aq}⁻ scavengers on the G(H₂) and in elucidating the fundamental mechanistic radiation chemistry of water. With the exception of a small number of results, data from these studies of γ-radiolysis are very consistent, implying that molecular hydrogen yields for nitrate and nitric acid solutions are not significantly different. At low nitrate concentrations G(H₂)_γ tends towards that for pure water G(H₂)_γ = 0.44 molecules (100 eV)⁻¹ (25 °C),¹⁵ but above ~0.01 mol dm⁻³ nitrate concentration G(H₂)_γ decreases until it is largely suppressed at sufficiently high concentrations, e.g. G(H₂)_γ = 0.02 molecules (100 eV)⁻¹ for 6 mol dm⁻³ nitrate. Throughout this work, radiolytic yields will be expressed as G-values quoted in the conventional radiation chemical unit of ions or molecules (100 eV)⁻¹, the corresponding S.I. unit is related by 1 ion or molecule (100 eV)⁻¹ = 0.104 μmol J⁻¹. In contrast, there are relatively few measurements of H₂ yields due to alpha (α-) radiolysis of nitrate and nitric acid solutions. This is due to the need for specialised facilities for safe handling of α-emitting radionuclides. Previous α-studies, also shown in Figure 1, used Pu (Table 1),^{10,16,17,18} ²¹⁰Po (τ_{1/2} = 138.376 days, 5.3 MeV α-particle),¹⁹ or ²⁴⁴Cm (τ_{1/2} = 18.10 years, 5.8 MeV α-particle)²⁰ as α-radiation sources in nitrate or nitric acid solutions, in some cases with the addition of sulfuric acid (H₂SO₄). The H₂ yields for α-radiolysis are larger than for γ-radiolysis as a consequence of the higher linear energy transfer (LET) of α-particles; higher LETs result in shorter radiation tracks with more closely spaced spurs in which second order processes favour molecular yields over radical yields.²¹ As is the case for γ-irradiation, increasing the nitrate concentration above 0.01 mol dm⁻³ decreases G(H₂)_α, resulting in almost complete suppression at sufficiently high nitrate concentrations. Alpha-irradiation data are particularly sparse at nitrate concentrations

below 1.0 mol dm^{-3} nitrate, which is the range most sensitive to nitrate concentration. Furthermore, the limiting H_2 yield at low nitrate concentrations should tend towards values of pure water or those for aqueous sulfuric acid solutions, but values reported in the literature show considerable scatter.^{20,22,23,24}

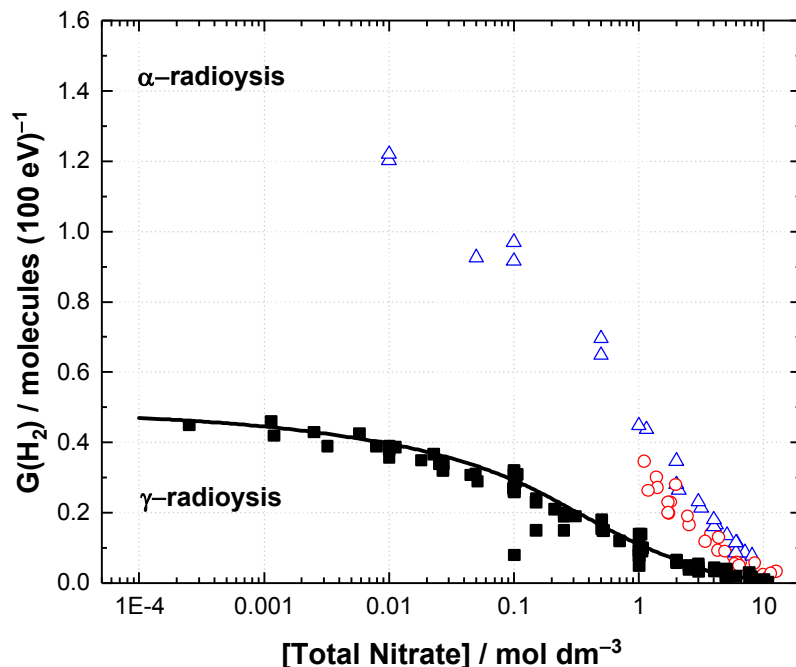


Figure 1. Comparison of available literature data for $G(H_2)$ from gamma (■)⁴⁻¹⁴ and alpha (plutonium ○¹⁰, polonium and curium △) radiolysis of aerated aqueous nitrate and nitric acid solutions. The solid curve is from stochastic radiation track calculations.²

Table 1. Isotopic composition of plutonium solutions used in previous studies.

Reference	²³⁸ Pu (%)	²³⁹ Pu (%)	²⁴⁰ Pu (%)	²⁴¹ Pu (%)	²⁴² Pu (%)
$\tau_{1/2}$ (years)	87.7	24114	6563	14.4	373500
α -particle (MeV)	5.49	5.15	5.16		4.89
Kazanjan <i>et al.</i> [10]	80				
Kazanjan <i>et al.</i> [16]	0.01	93.72	5.86	0.39	0.022
Sheppard [17]	0.03	Balance	7.5-8.4		
Kuno <i>et al.</i> [18]	1.17	62.83	23.51	8.46	4.01
	0.0037	74.37	19.50	4.22	1.88

Early measurements by Lefort^{25,26} using ²²²Rn ($\tau_{1/2}$ = 3.82 days, 5.5 MeV α -particle) or ²¹⁰Po as an α -source gave $G(H_2)_\alpha$ between 1.7 and 1.8 under both aerated and deaerated conditions for pure water, as well as acidic and alkaline solutions, whereas Senvar and Hart²⁷ measured $G(H_2)_\alpha$ = 1.45 using ²¹⁰Po as an external source. These $G(H_2)_\alpha$ values compare with measurements

obtained using cyclotron 5 MeV helium ion ($^4\text{He}^{2+}$) irradiation, $G(\text{H}_2)_a = 1.2\text{--}1.3$ for deaerated pure water.^{28,29} There is some concern over utilising particle accelerators as a substitute for radionuclide studies: $^4\text{He}^{2+}$ beams from accelerators normally deliver very high local dose-rates due to the ion currents used and the very small penetration of the ions into the target solution. For instance, 5.5 MeV $^4\text{He}^{2+}$ ions, which are of comparable energy to α -emission from plutonium and americium, have a range in water of $\sim 44\text{ }\mu\text{m}$ ³⁰, so at 1 nA current and 0.5 cm beam diameter an ion beam delivers a dose rate of 10 MGy hr^{-1} in the irradiated volume; this compares with 6×10^{-6} to $6 \times 10^{-4}\text{ MGy hr}^{-1}$ for the plutonium solutions used in this study. Consequently, the validity of comparing radionuclide and accelerator $^4\text{He}^{2+}$ ion beams studies based on average solution dose rates may be questioned.³¹

The present work investigates the H_2 yields from the α -radiolysis of aerated aqueous nitric acid solutions through a combination of experimental studies using the self-radiolysis of plutonium and americium nitric acid solutions combined with stochastic radiation track modelling calculations. The main focus of these experiments was to: (i) provide greater insight into the α -radiolytic production of H_2 from nitric acid solutions with concentrations below 1 mol dm^{-3} , as this is where the H_2 yields have the greatest uncertainty; and (ii) determine whether or not $G(\text{H}_2)_a$ is subject to significant dose rate effects, i.e. whether particle accelerator studies are a representative and viable alternative to studies using radionuclides.

MATERIALS AND METHODS

Experimental

Chemicals. Nitric acid (99.995 % trace metals basis), sulfuric acid (Certified ACS grade), and sodium hydroxide (Certified ACS grade) were supplied by Fisher Scientific. Plutonium and americium nitrate were supplied by the National Nuclear Laboratory. The plutonium isotopic distribution of the plutonium nitrate and plutonium sulphate solutions were measured by mass spectrometry and corrected for subsequent radioactive decay of plutonium and ingrowth of ^{241}Am ($^{241}\text{Pu} \rightarrow ^{241}\text{Am} + \beta^- + \bar{\nu}$, $\tau_{1/2} = 14.4$ years). The calculated isotopic distributions of the stock solutions at the time of these experiments are given in **SI Table 1**. All chemicals were used as received without further purification. Ultra-pure water was used to make up all aqueous solutions.

Actinide Solution Preparation. The composition of plutonium (**Pu1–Pu33**) and americium nitrate solutions (**Am1–Am7**) are detailed in Tables 2 and 3 of the **Supporting Information (SI)**. Three series of plutonium experiments were performed: **Pu1–Pu11** varied nitrate concentration between 0.1–1.3 mol dm⁻³ at approximately constant plutonium concentration (~50 mM); **Pu12–Pu29** varied plutonium concentration at 1.6, 1.6, and 160 mM and varied nitrate concentrations at approximately 2.5, 0.25 and 5×10^{-2} mol dm⁻³; **Pu30–Pu33** maintained constant plutonium concentration (~0.24 mM) and varied nitric acid concentration between 0.1 – 6.0 mol dm⁻³. Reducing the acidity below 1 mol dm⁻³ H_{aq}⁺ tends to hydrolyse and precipitate plutonium, particularly below 0.1 mol dm⁻³ H_{aq}⁺.³² For this reason, measurements for solutions with nitrate concentrations <0.8 mol dm⁻³ used solutions of plutonium sulphate in sulfuric acid with the appropriate nitrate concentration added.

Plutonium nitrate solutions were prepared by small additions of concentrated nitric acid to diluted stock solutions of plutonium(IV) nitrate. Plutonium sulphate solutions were made by neutralising plutonium(IV) nitrate with sodium hydroxide solution to precipitate plutonium(IV) hydroxide. The precipitate was washed and dissolved in 2.2 mol dm⁻³ sulfuric acid (**Pu1–Pu9**) or 0.75 mol dm⁻³ sulfuric acid (**Pu18–Pu29**). The precipitation, washing, and dissolution steps were repeated. For experiments with mixed nitrate and sulphate solutions, small volumes of concentrated nitric and sulfuric acid were added to the plutonium sulphate solutions and diluted to the appropriate volume. Americium solutions were prepared by dilution of an americium nitrate stock solution of purity >99 % ²⁴¹Am ($\tau_{1/2}$ = 432.2 years, 5.637 MeV) with small volumes of concentrated nitric and sulfuric acid. Low nitrate concentration solutions (**Am1–Am3**) had 0.75 mol dm⁻³ sulfuric acid added for consistency with the corresponding plutonium experiments. In all cases the solutions were aerated and solution volumes were 0.5 mL except experiments **Pu30–Pu33** and **Am4–Am7** where 5 mL was used.

Hydrogen Yield Measurements. Molecular hydrogen production was generally determined by repeatedly sampling the headspace gas of each vessel over time, replacing the sampled gas with laboratory air. However, in a small number of experiments (**Pu30–33** and **Am4–Am7**, indicated by asterisk in **SI Tables 1** and **2**) H₂ production was determined by preparing several identical vessels that were each sampled only once at different times. Molecular hydrogen concentrations were measured by gas chromatography using an Agilent Micro Gas Chromatograph-3000 (μGC) operating with a single channel molsieve 5 Å column,

thermal conductivity detector and argon carrier gas. $G(\text{H}_2)$ values were determined from the slope of the H_2 produced *vs.* time plots, for example see **SI Figure 1**, and the total α -dose rate to the solution. Molecular hydrogen was generated at a constant rate over the duration of measurements. The α -dose rates were calculated from the respective activities of the actinide solutions and were corrected for decay of the various isotopes and the ingrowth of additional radionuclides. Uncertainties in $G(\text{H}_2)_\alpha$ were estimated from the standard error in the slope of H_2 production *vs.* time, with uncertainty in the plutonium and americium concentration and the isotopic composition being taken to be small, and error bars are plotted as the 95 % confidence interval.

Stochastic Radiation Track Simulations

Radiation track simulations used a stochastic modelling code which has been described in detail previously.³³ Both γ - and α -radiolysis track simulations were performed for aerated ($[\text{O}_2] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$) aqueous nitric acid solutions. For the α -simulations an array of energies were simulated (0.1–6 MeV), and the resulting H_2 yields were then integrated to 5 MeV to derive the presented $G(\text{H}_2)_\alpha$ values. The simulations followed the evolution of the radiation track up to 1 μs to allow for complete spatial relaxation. Direct radiation effects on nitrate and nitric acid were not included in track calculations as their products (NO_3^\bullet , e^- , HNO_2 , NO_2^- , and $\text{O}(^3\text{P}/^1\text{D})$) do not impinge upon the radiolytic yield of H_2 . This is because at the total nitrate concentrations that coincide with direct radiolysis ($\geq 1 \text{ mol dm}^{-3}$) the majority of H_2 is formed through the decomposition of excited state water (H_2O^*) and not through inter/intra-track chemistry.

RESULTS

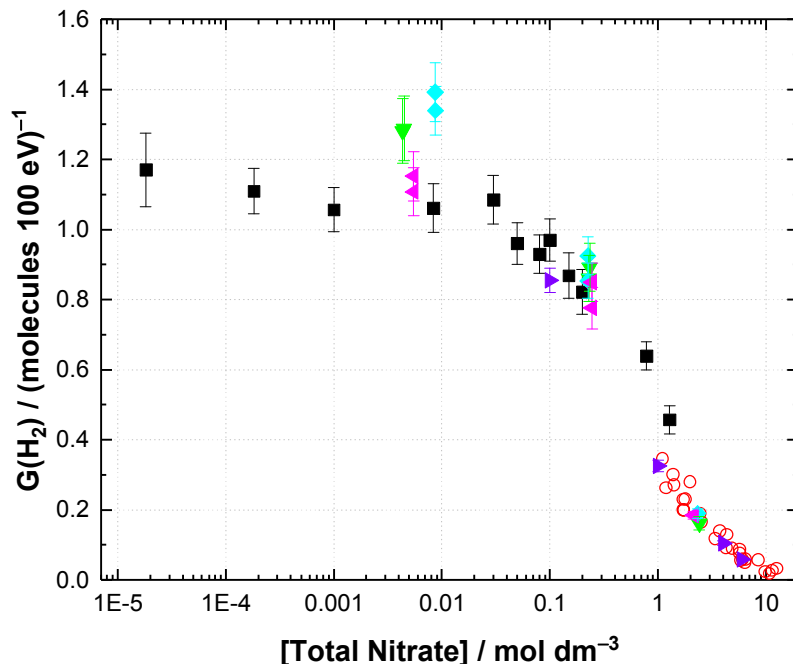


Figure 2. $G(\text{H}_2)_\alpha$ from self-radiolysis by plutonium in nitric acid solutions as a function of total nitrate concentration for plutonium concentrations: 50 mM (■), 1.6 mM (▼), 16 mM (◆), 160 mM (◀), 0.24 mM (▶), and the available plutonium literature (○)¹⁰. Error! Bookmark not defined.

Figure 2 and 3 summarise the $G(\text{H}_2)_\alpha$ yields from self-radiolysis by plutonium and americium in nitric acid solutions as a function of total nitrate in solution. As with the previously shown γ -radiolysis data, $G(\text{H}_2)_\alpha$ decreases with increasing nitric acid concentration for both plutonium and americium solutions. These $G(\text{H}_2)_\alpha$ values are in good agreement with the literature data for plutonium solutions in the 1–10 mol dm⁻³ nitrate concentration range.^{Error!}

^{Error!} At lower nitrate concentrations (<0.01 mol dm⁻³), greater variation in the results was observed with $G(\text{H}_2)_\alpha$ values for lower plutonium concentrations of 1.6 and 16 mM being higher than for higher plutonium concentrations of 50 and 160 mM, indicating that plutonium ions may have a modest influence on the radiolytic generation of H_2 in this HNO_3 concentration regime.

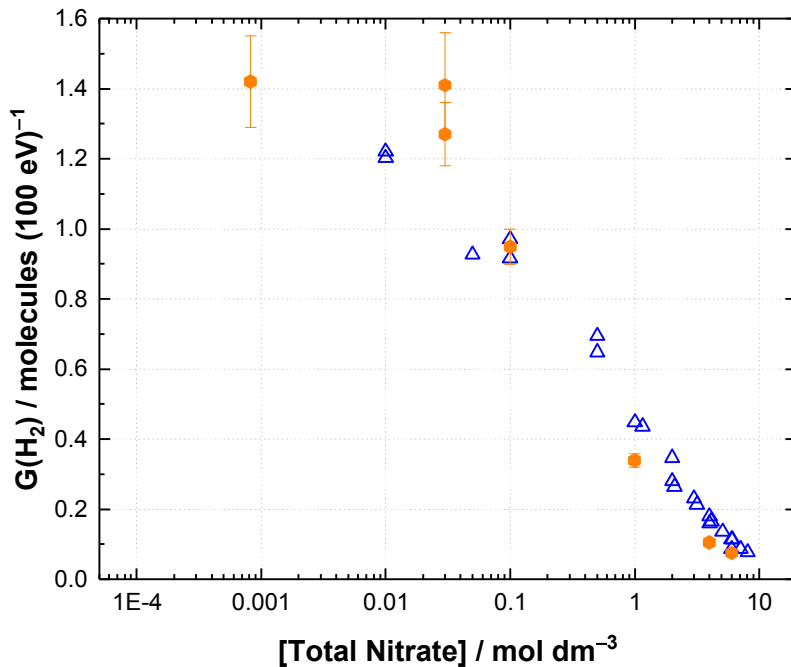


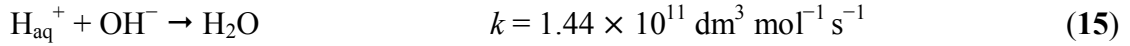
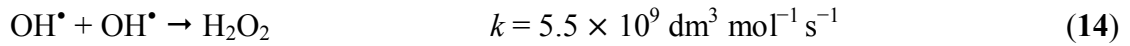
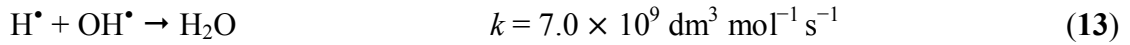
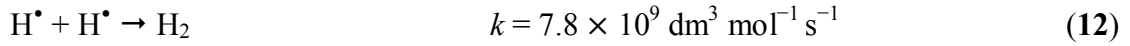
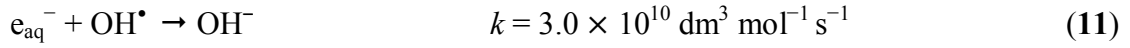
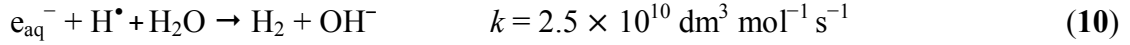
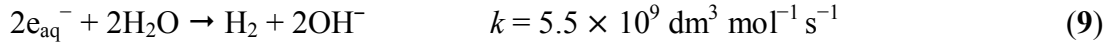
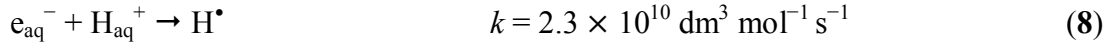
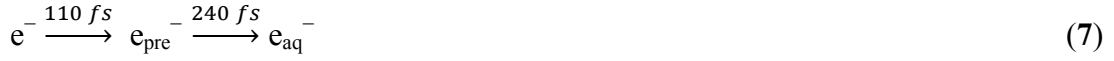
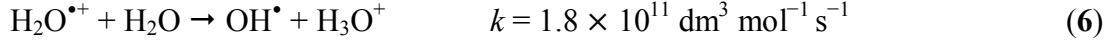
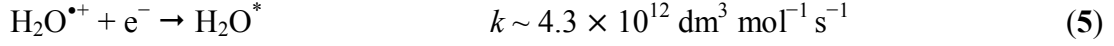
Figure 3. $G(H_2)_\alpha$ from self-radiolysis by americium in nitric acid solutions as a function of total nitrate concentration: 1.6 mM ^{241}Am (●) and the available polonium and curium (△). Error! Bookmark not defined., Error! Bookmark not defined.

The $G(H_2)_\alpha$ values for americium solutions are in very good agreement with those from the corresponding plutonium data between 1 and 10 mol dm⁻³, falling systematically below data reported for curium and polonium solutions. For lower nitrate concentrations, the americium $G(H_2)_\alpha$ values are closer in agreement to the higher values measured for low plutonium concentration solutions shown in **Figure 2**. Comparison of the $G(H_2)_\alpha$ values for these two radionuclides at low nitrate concentrations indicates a limiting H_2 yield between 1.2 and 1.4, in agreement with measurements obtained using cyclotron 5 MeV $^4\text{He}^{2+}$ irradiation.^{28,29}

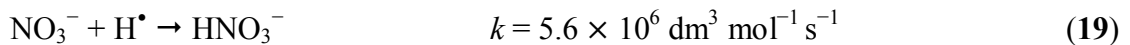
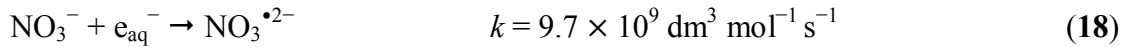
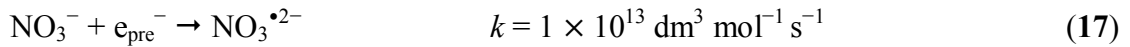
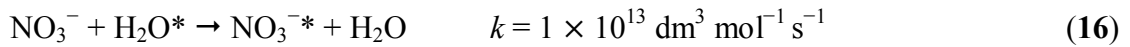
DISCUSSION

Effect of Nitrate Concentration on Molecular Hydrogen Yield. The initial chemistry in the radiolysis of water is generally agreed to proceed via reactions **1–15**.^{2,15,21,34,35,36}





Although reactions **8–10** are important in determining $G(\text{H}_2)$ from aqueous solution,²⁸ the greatest contribution (>70 %) comes from the fragmentation of H_2O^* (reaction **4**), produced by either direct excitation (reaction **2**) or recombination (reaction **5**). The decrease in $G(\text{H}_2)$ in aqueous solutions of nitrate is a consequence of NO_3^- quenching and scavenging the precursors to H_2 (i.e. H_2O^* , e_{pre}^- , e_{aq}^- , and H^\bullet).^{2,36-38}



Stochastic radiation track calculations for the γ -irradiation of aerated aqueous nitrate solutions, including both quenching and scavenging processes, are included in Figure 1 and are in very

good agreement with the corresponding experimental data for both nitrate and nitric acid solutions.²

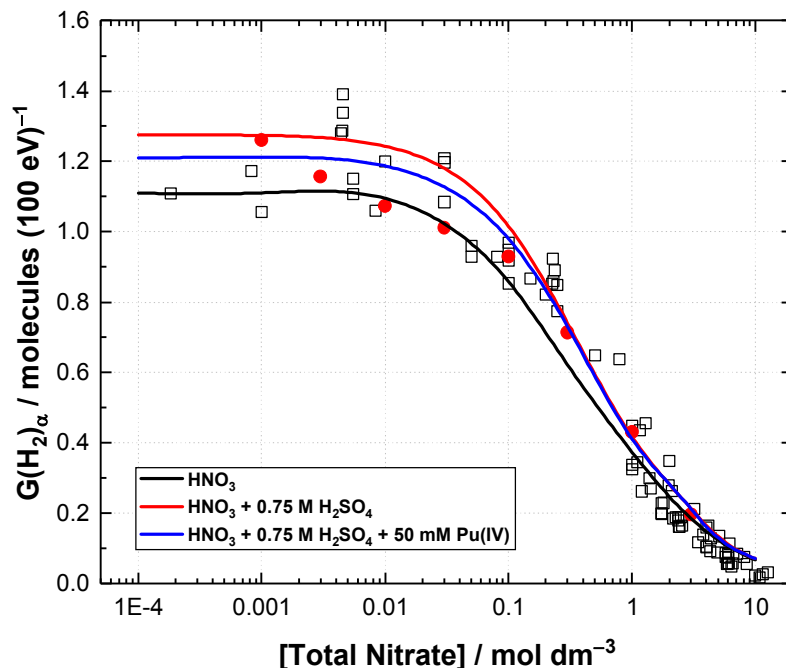


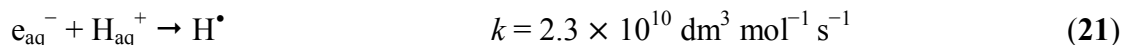
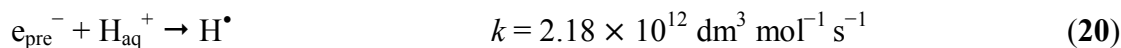
Figure 4. $G(\text{H}_2)_\alpha$ as a function of total nitrate concentration: α -radiolysis of HNO_3 solutions for self-radiolysis by Am, Cm, Po, and Pu (\square)¹⁰, as shown in **Figure 2** and **Figure 3**; 5 MeV He^{2+} ion radiolysis of deaerated aqueous NO_3^- (\bullet)³⁹ solutions. Solid curves are for stochastic calculations for HNO_3 (**Black Curve**), $\text{HNO}_3 + 0.75 \text{ M H}_2\text{SO}_4$ (**Red Curve**), and $\text{HNO}_3 + 0.75 \text{ M H}_2\text{SO}_4 + 50 \text{ mM Pu(IV)}$ (**Blue Curve**).

Modelling has been extended to the case of 5 MeV α -irradiation of aerated solutions of nitric acid, covering the experimental conditions used in this work and in deaerated nitrate solutions from previous ion accelerator studies.³⁹ The results are plotted in **Figure 4** alongside the previously discussed experimental data, as a function of total nitrate concentration. The $G(\text{H}_2)_\alpha$ values from the stochastic calculations are in good agreement with the corresponding experimental data. With regards to aerated solutions of HNO_3 , the yields of the α -radiation track reactions responsible for H_2 formation as a function of HNO_3 concentration are given in Table 2, along with their calculated radiolytic yields. In pure water, the two most important H_2 production pathways are dissociation of H_2O^* (reaction 4) and the reaction of the e_{aq}^- with H^\bullet (reaction 10).

Table 2. Calculated α -radiation track reaction yields for reactions producing molecular hydrogen from aerated water and aerated nitric acid (1×10^{-4} to 10 mol dm^{-3}), taken at $1 \mu\text{s}$ for a 3 MeV He^{2+} ion (Mean LET = $1.44 \times 10^2 \text{ eV nm}^{-1}$).

Reaction	Aerated Water	[HNO ₃] (mol dm ⁻³)					
		10 ⁻⁴	10 ⁻³	10 ⁻²	10 ⁻¹	1	10
$2e_{\text{aq}}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^-$ (9)	0.11	0.10	0.09	0.08	0.04	0.00	0.00
$e_{\text{aq}}^- + \text{H}^\bullet + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^-$ (10)	0.31	0.31	0.29	0.19	0.06	0.00	0.00
$\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2$ (12)	0.07	0.06	0.11	0.18	0.14	0.05	0.03
$\text{H}_2\text{O}^* \rightarrow \text{O}(^3\text{P}/^1\text{D}) + \text{H}_2$ (4)	0.62	0.64	0.62	0.66	0.56	0.34	0.08

As the acidity of the solution increases with HNO₃ concentration, the yield of reaction **12** increases going from 0.07 in pure water to 0.18 at $1 \times 10^{-2} \text{ mol dm}^{-3}$ HNO₃, which corresponds to a change in pH from ~ 7 to 2. This is a consequence of the presence of H_{aq}^+ which has long been noted as an effective scavenger of both e_{pre}^- and e_{aq}^- (reactions **20** and **21**, respectively).³⁴



For HNO₃ concentrations below the threshold for scavenging e_{pre}^- , H_{aq}^+ scavenges $\sim 70\%$ of the e_{aq}^- that in a nitrate solution of neutral pH would be scavenged by NO_3^- , as shown in Table 3. This leads to the formation of higher concentrations of H^\bullet , which reacts almost three magnitudes slower with NO_3^- than e_{aq}^- . Consequently, more e_{aq}^- is converted to H_2 via H^\bullet , albeit dissolved O_2 scavenges a notable fraction of the additional H^\bullet . This condition is maintained until the concentration of NO_3^- is sufficiently high to begin quenching H_2O^* and scavenging e_{pre}^- . With regards to the latter, NO_3^- is a more effective scavenger than H_{aq}^+ , consuming $\sim 82\%$ of the e_{pre}^- that would be scavenged by NO_3^- , relative to complementary neutral pH nitrate solutions

Table 3. Percentage partitioning of e_{aq}^- and e_{pre}^- between NO_3^- and H_{aq}^+ in aqueous HNO_3 as a function of their respective scavenging capacities.

Reaction	Percentage Partitioning (%)
$H_{aq}^+ + e_{pre}^- \rightarrow H^\bullet$	17.90
$NO_3^- + e_{pre}^- \rightarrow NO_3^{\bullet 2-}$	82.10
$H_{aq}^+ + e_{aq}^- \rightarrow H^\bullet$	70.34
$NO_3^- + e_{aq}^- \rightarrow NO_3^{\bullet 2-}$	29.66

Table 4 gives the calculated radiolytic yields of the α -radiation track reactions responsible for inhibiting H_2 formation as a function of HNO_3 concentration. At low HNO_3 concentrations, $G(H_2)_\alpha$ is controlled by the reactions of e_{aq}^- and H^\bullet with OH^\bullet and O_2 , and to a lesser extent by H_2O_2 with e_{aq}^- ; therefore, in the absence of oxygen the accelerator studies give a higher yield at the low nitrate concentration limit than the radionuclide experiments in aerated nitric acid. As the concentration of HNO_3 increases, scavenging of e_{aq}^- by nitrate becomes increasingly important, balancing the increased significance of reaction **12** and **21** so that there is no change in the yield of H_2 up to $1 \times 10^{-2} \text{ mol dm}^{-3} HNO_3$. At higher nitrate concentrations quenching and scavenging of H_2O^* , e_{pre}^- and H^\bullet become the main reactions of inhibiting H_2 formation.

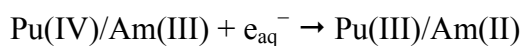
Table 4. Calculated α -radiation track reaction yields, for the most important reactions inhibiting molecular hydrogen production from aerated water and aerated nitric acid (1×10^{-4} to 10 mol dm^{-3}), taken at $1 \text{ }\mu\text{s}$ for a 3 MeV He^{2+} ion (Mean LET = $1.44 \times 10^2 \text{ eV nm}^{-1}$).

Reaction	Aerated Water	[HNO ₃] (mol dm ⁻³)					
		10 ⁻⁴	10 ⁻³	10 ⁻²	10 ⁻¹	1	10
$e_{\text{aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{OH}^\bullet$	0.44	0.40	0.30	0.13	0.01	0.00	0.00
$e_{\text{aq}}^- + \text{O}(^3\text{P}) \rightarrow \text{O}^{\bullet-}$	0.07	0.05	0.04	0.03	0.01	0.00	0.00
$e_{\text{aq}}^- + \text{HO}_2^\bullet \rightarrow \text{HO}_2^-$	0.02	0.02	0.01	0.00	0.00	0.00	0.00
$\text{H}^\bullet + \text{O}(^3\text{P}) \rightarrow \text{OH}^\bullet$	0.03	0.03	0.02	0.05	0.03	0.02	0.00
$\text{H}^\bullet + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2$	0.04	0.05	0.09	0.08	0.06	0.02	0.01
$\text{OH}^\bullet + e_{\text{aq}}^- \rightarrow \text{OH}^-$	0.98	1.02	0.90	0.49	0.08	0.00	0.00
$\text{OH}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2\text{O}$	1.08	1.06	1.11	1.24	1.34	0.73	0.29
$\text{O}_2 + e_{\text{aq}}^- \rightarrow \text{O}_2^{\bullet-}$	0.37	0.29	0.11	0.04	0.00	0.00	0.00
$\text{O}_2 + \text{H}^\bullet \rightarrow \text{HO}_2^\bullet$	0.42	0.52	0.68	0.80	0.69	0.38	0.15
$\text{NO}_3^- + e_{\text{pre}}^- \rightarrow \text{NO}_3^{\bullet 2-}$	0.00	0.00	0.01	0.10	0.89	2.51	2.75
$\text{NO}_3^- + e_{\text{aq}}^- \rightarrow \text{NO}_3^{\bullet 2-}$	0.00	0.06	0.20	0.57	0.68	0.17	0.00
$\text{NO}_3^- + \text{H}^\bullet \rightarrow \text{HNO}_3^-$	0.00	0.00	0.00	0.00	0.02	0.07	0.26
$\text{NO}_3^- + \text{H}_2\text{O}^* \rightarrow \text{NO}_3^* + \text{H}_2\text{O}$	0.00	0.00	0.00	0.03	0.30	1.55	2.79

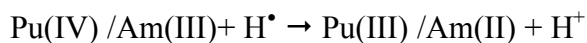
Actinide solutions were prepared in sulfuric acid solution for low HNO₃ concentrations ($<0.1 \text{ mol dm}^{-3}$). Under these conditions $G(\text{H}_2)_\alpha$ is higher than calculated for pure HNO₃ solutions but has similar insensitivity up to $1 \times 10^{-2} \text{ mol dm}^{-3}$ HNO₃. In this case, scavenging of e_{aq}^- by H_{aq}^+ is dominant until nitrate reaches $1 \times 10^{-2} \text{ mol dm}^{-3}$ and effectively competes for scavenging of precursors to H₂ and reduces $G(\text{H}_2)_\alpha$. The higher yield of H₂ from acidic solutions is consistent with analysis by Schwarz *et al.* who measured a higher yield from sulfuric acid vs. water at high LET.⁴¹ Valdimirova also measured $G(\text{H}_2)_\alpha$ increasing from 1.37 to 1.55 for the dose to water between 0.4 and 4 mol dm⁻³ H₂SO₄ using ²¹⁰Po α -irradiation.⁴² The observed increasing yield with acidity for α -radiolysis differs from low LET γ -irradiation where, the $G(\text{H}_2)_\gamma$ is well established to decrease only slightly from about 0.44 in pure water to 0.41 in

0.4 mol dm⁻³ H₂SO₄ at room temperature.^{3,43} This is a consequence of LET effects promoting greater recombination of H[•] to H₂, relative to gamma tracks.

Effect of Plutonium and Americium Concentration. Plutonium and americium are redox active and may react with species generated from the radiolysis for water. Of potential importance are the reactions of Pu(IV)/Am(III) with the precursors to H₂, for example reactions **22** and **23**. For these reactions to have a significant effect on G(H₂)_α they would need to be competitive with scavenging by nitrate ions (reactions **16–19**). Rates coefficients for the reaction of Pu(IV) and Am(III) with the e_{aq}⁻ and H[•] have been reported.^{44,45}



$$\begin{aligned} k_{\text{Pu(IV)}} &= 4.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} & (0.04 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4) \\ k_{\text{Am(III)}} &= 2.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} & (\text{pH } 6) \end{aligned} \quad (22)$$



$$k_{\text{Pu(IV)}} = 4.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (0.6 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4) \quad (23)$$

During preparation of solutions with lower acid concentrations disproportionation of Pu(IV) to Pu(III) and Pu(VI) will have occurred, reducing the potential role of reactions 22 and 23.

Preliminary calculations including these reactions of plutonium, shown in Figure 4 for 50 mM Pu(IV) in solution, suggest that the reduction of Pu(IV) to Pu(III) may influence radiation track chemistry at HNO₃ concentrations below 0.1 mol dm⁻³. The decrease in G(H₂)_α, relative to the corresponding HNO₃ + 0.75 mol dm⁻³ H₂SO₄ system, at 1 × 10⁻⁴ mol dm⁻³ nitrate is directly related to Pu(IV) scavenging e_{aq}⁻, reaction **22**. The agreement is not exact, but a more complete model of the plutonium redox chemistry, and inclusion of reactions with other water radiolysis species, would be needed to refine the understanding of this system. The much lower concentration of americium than plutonium used in experiments, together with its lower reaction rate with e_{aq}⁻, implies it will not have a significant effect on H₂ production.

Measurements in the range of 1 and 10 mol dm⁻³ total nitrate showed no significant effect of plutonium concentration between 24 and 160 mM on G(H₂)_α and data obtained from americium solutions were also consistent with plutonium solution measurements rather than

tending towards the yields for ^{244}Cm and ^{210}Po solutions. These results imply no significant effect of plutonium redox chemistry on the molecular hydrogen yield. This is consistent with the findings of Bibler^{Error! Bookmark not defined.} who added 209 mM ^{239}Pu ($\tau_{1/2} = 24110$ years, 5.15 MeV α -particle) to ^{244}Cm solutions and did not observe a significant effect on the yield, although $G(\text{H}_2)_\alpha$ appears systematically higher than for plutonium solutions. In contrast, Kuno *et al.*^{Error! Bookmark not defined.} reported a significant decrease in $G(\text{H}_2)_\alpha$ as plutonium concentration was increased from 41 to 670 mM for solution with 1 and 10 mol dm⁻³ total nitrate. By extrapolating their data to zero plutonium concentration they found agreement with experiments of Bibler^{Error! Bookmark not defined.} using ^{244}Cm as the radiation source and proposed that scavenging of e_{aq}^- or its precursors by plutonium explained the lower yield measured in plutonium solutions. For scavenging of precursors to H_2 by plutonium to be significant between 1 and 10 mol dm⁻³ HNO_3 the rate of reaction with e_{pre}^- or quenching of H_2O^* would need to be competitive with the reactions of nitrate. No information on these rates is available, but since the concentration of plutonium is much less than nitrate in these experiments the rate coefficients would need to be of much greater magnitude than those for nitrate to significantly contribute. Consequently, the difference in $G(\text{H}_2)_\alpha$ for experiments using plutonium and ^{244}Cm and remains unexplained.

Comparison of Radionuclide and Accelerator Experiments. As outlined earlier, concerns have been raised regarding the use of accelerator experiments for replicating radionuclide α -decay irradiations, owing to the very high local dose rates inherent in accelerator studies.³¹ The radionuclide experiments and stochastic calculations presented show little difference in $G(\text{H}_2)_\alpha$ relative to the corresponding accelerator experiments. As there is little difference between the $G(\text{H}_2)_\alpha$ values from accelerator and radionuclide experiments, it may be concluded that these two approaches to investigating the effects of α -irradiation on matter are equivalent; at the very least in terms of H_2 production from aqueous solutions. Furthermore, the results from the stochastic calculations are important for resolving this matter, as they reflect the limiting low dose, isolated track regime and, therefore, any significant effects attributed to dose rate would have become apparent in the calculated yields, which is not the case. Consequently, concerns attributed to the overlapping of tracks and/or non-homogeneous energy distribution through the use of very high local dose rates by accelerator studies may be considered to be unfounded with respect to the radiolytic formation of H_2 . This is not to say that dose rate effects do not play a part in the evolution of other water radiolysis species.

On the other hand, the data presented show the challenges of using radionuclide studies to provide insight into radiation effects when using redox active metals, such as plutonium. At sufficiently high concentrations, redox active metals are able to influence the chemistry of an irradiated solution and in doing so alter the yields of observable radiolytic products.^{46,47,48} Preliminary calculations performed as part of this work, given in **Figure 4**, provide evidence for plutonium's influence on radiation track chemistry at low nitric acid concentrations ($\leq 1 \times 10^{-3} \text{ mol dm}^{-3}$).

CONCLUSIONS

Measurements of $G(\text{H}_2)_\alpha$ from self-radiolysis by plutonium and americium containing solutions of aqueous nitric and its mixtures with sulfuric acid have been compared with radiation track modeling calculations. These show measurable differences in the variation of molecular hydrogen yield with nitrate concentration for pure nitric acid and nitric acid-sulfuric acid solutions, not seen for gamma irradiation. The differences can be explained using the prediction of stochastic radiation track models as resulting from scavenging of the e_{aq}^- by H_{aq}^+ to form H^\bullet . While plutonium has been shown to be an effective scavenger of precursors of molecular hydrogen below 0.1 mol dm^{-3} nitrate, previously reported effects of plutonium on $G(\text{H}_2)_\alpha$ between 1 and 10 mol dm^{-3} nitric acid were not reproduced. Comparison between the radionuclide and accelerator experiments and model predictions leads to the conclusion that the high dose rate of accelerator studies does not significantly affect the measured $G(\text{H}_2)_\alpha$.

Validation of the stochastic radiation track modelling for α -irradiation of nitric acid solutions against experimental $G(\text{H}_2)_\alpha$ values is the precursor to its use in more sophisticated multi-scale modelling involving bulk homogeneous reactions and plutonium redox chemistry, which recent studies have shown to be important in determining radiation chemical behaviour.⁴⁶ From a practical perspective the data presented are relevant to safety assessments of laboratory wastes, reprocessing, and minor actinide partitioning flowsheets at higher plutonium concentrations,^{49,50} such as proposed for the "EURO-GANEX" flowsheet⁵¹ and also mixed oxide fuels reprocessing.⁵²

SUPPORTING INFORMATION

Details of experimental samples (pdf)

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