Hydrogen yields from plutonium alpha-radiolysis of nitrate solutions

SACSESS International Workshop
24th April 2015

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Background

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- Nitric acid is used widely within the nuclear industry:
  - Dissolution of spent nuclear fuel
  - Reprocessing facilities
  - Analytical processes
  - POCO and decommissioning operations

- Hydrogen production from radiolysis of aqueous solutions is a potential hazard:
  - Flammable gas mixtures
  - Pressurisation

- Relevant to safety studies of reprocessing flowsheets at higher plutonium concentrations e.g. GANEX and mixed oxide fuel reprocessing

Water radiolysis: Hydrogen production

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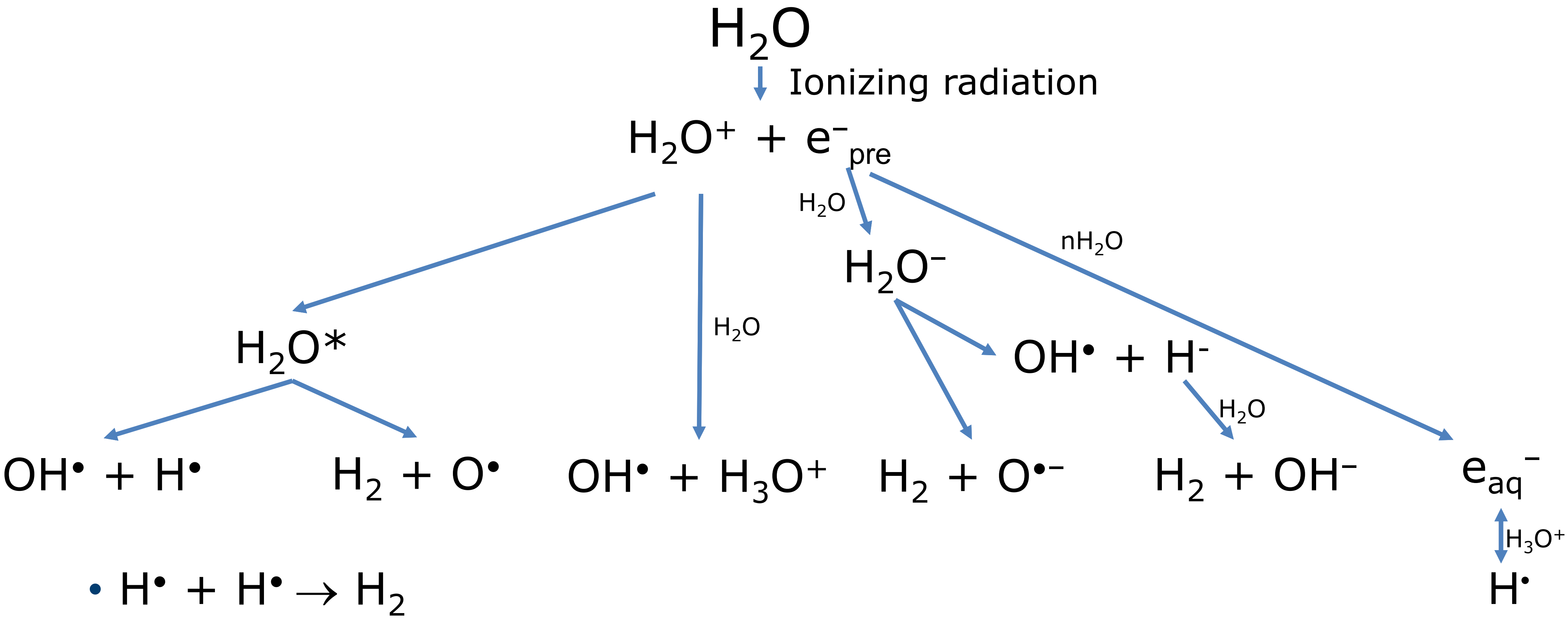
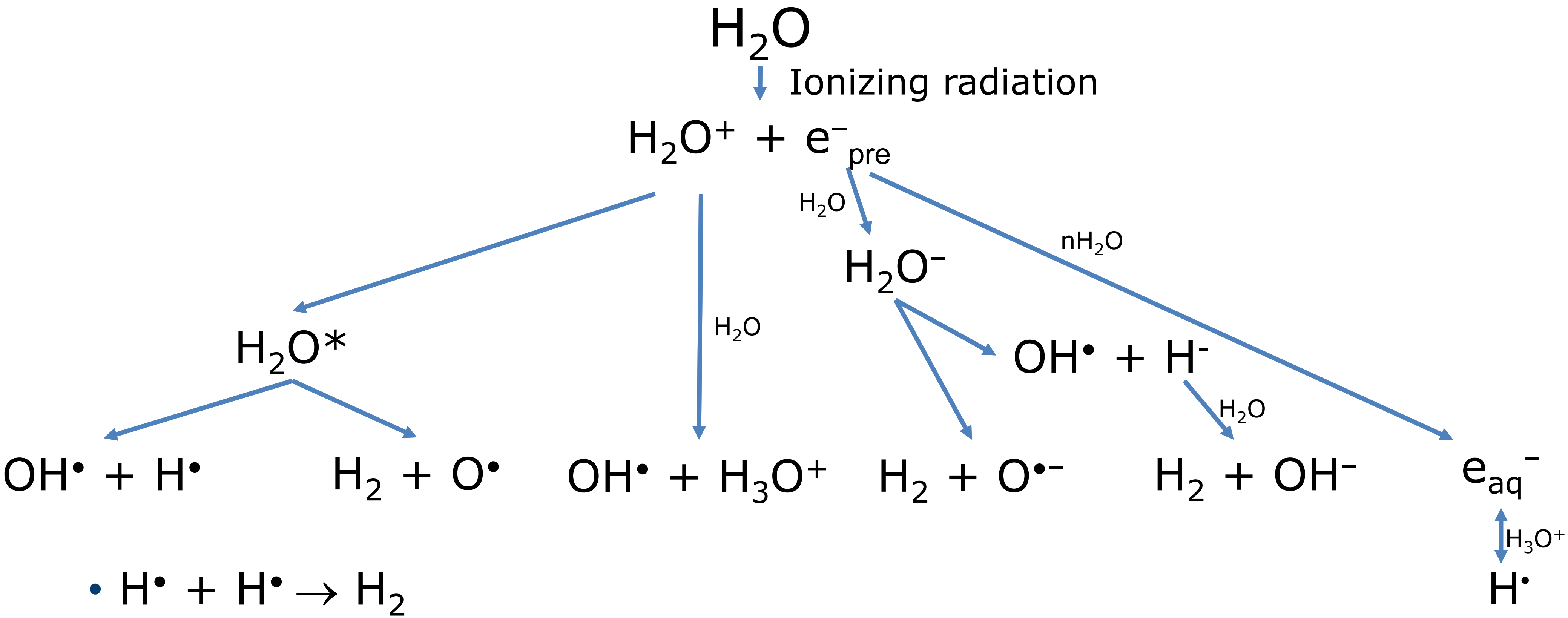


- $H^\bullet + H^\bullet \rightarrow H_2$
- $e_{aq}^- + e_{aq}^- \ (+2H_2O) \rightarrow H_2 + 2OH^-$
- $e_{aq}^- + H^\bullet + H_2O \rightarrow H_2 + 2OH^-$

- Removal of hydrogen by $OH^\cdot$
  - $OH^\cdot + H_2 \rightarrow H^\cdot + H_2O$

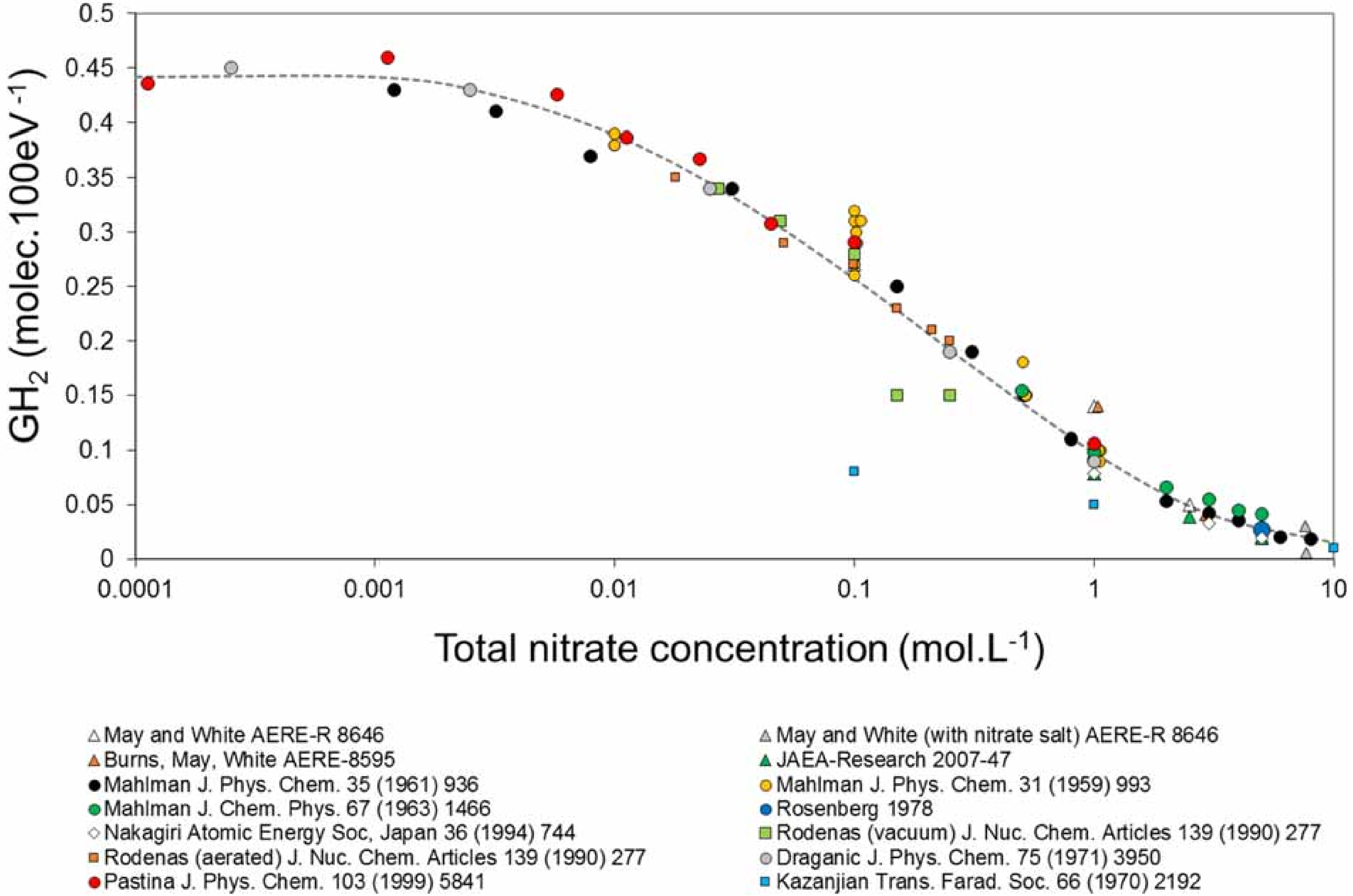
Water radiolysis: Hydrogen production and the effect of nitrate



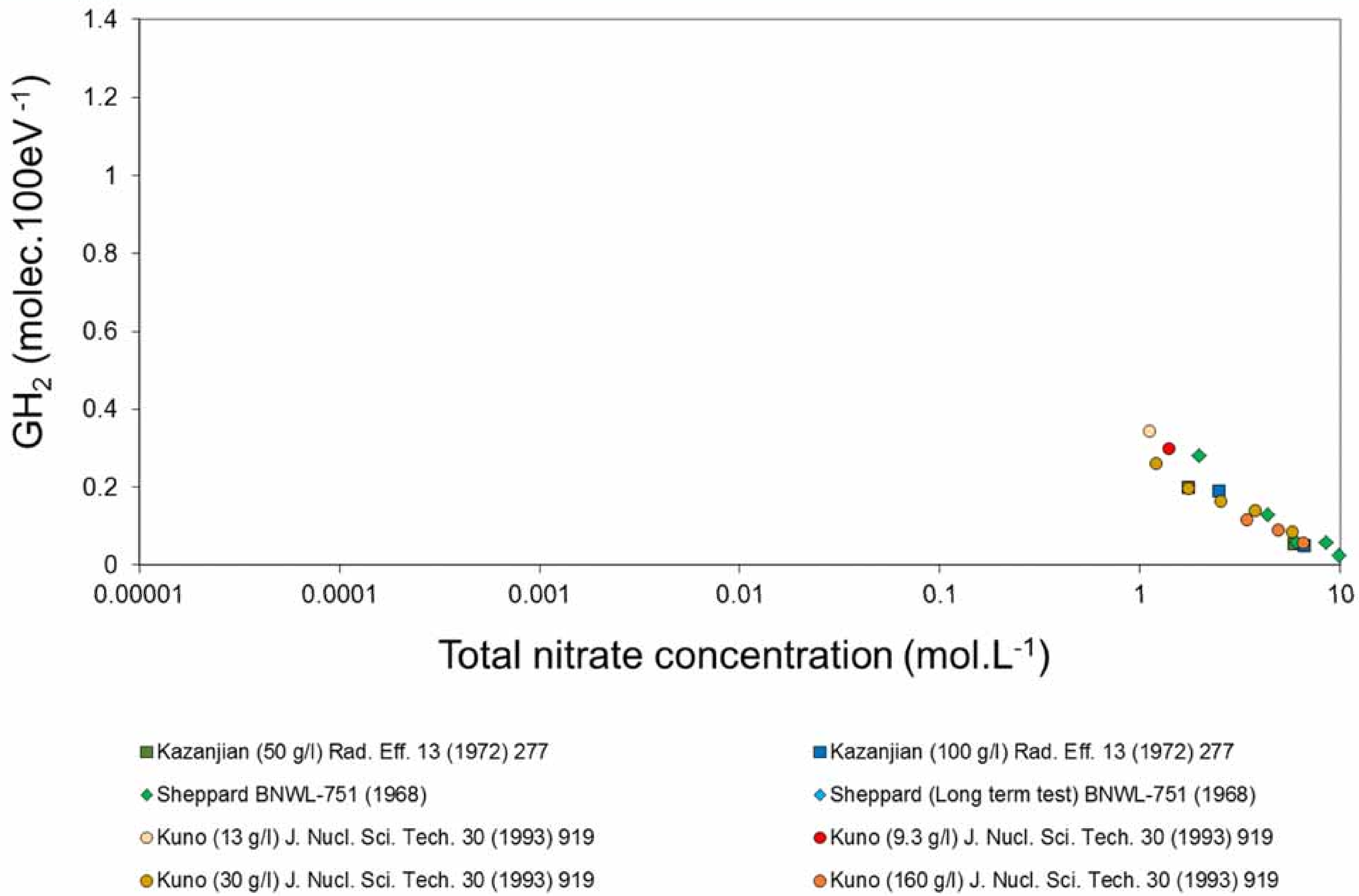
- $H^{\bullet} + H^{\bullet} \rightarrow H_2$
- $e_{aq}^{-} + e_{aq}^{-}\ (+2H_2O) \rightarrow H_2 + 2OH^{-}$
- $e_{aq}^{-} + H^{\bullet} + H_2O \rightarrow H_2 + 2OH^{-}$

- Scavenging of the precursors of H_2
  - $e^{-}_{pre/aq} + NO_3^{-} \rightarrow NO_3^{2-}$ $H^{\bullet} + NO_3^{-} \rightarrow NO_3^{2-} + H^{+}$

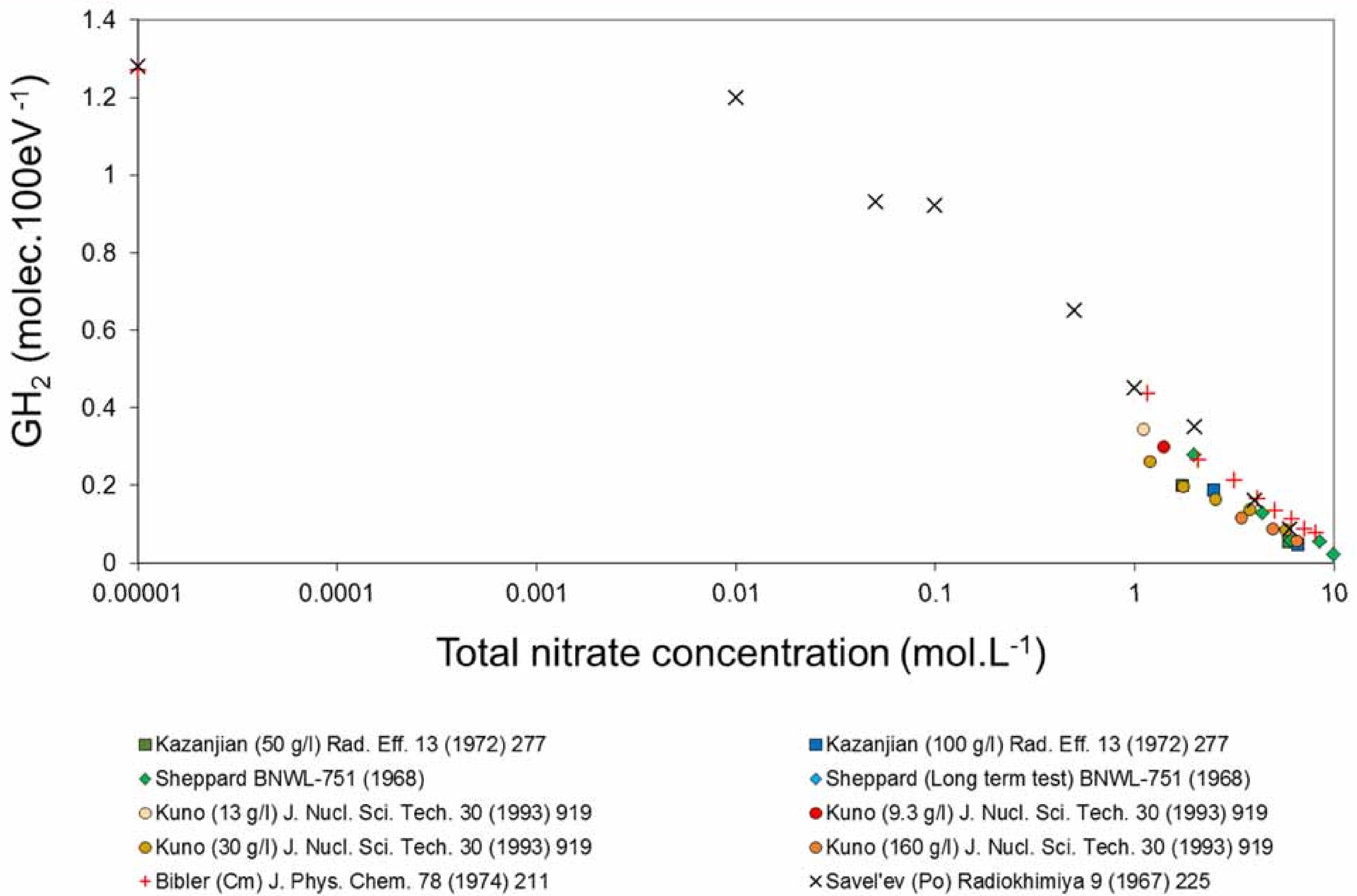
Literature: Gamma radiolysis of nitrate and nitric acid solutions



Literature: Pu alpha radiolysis of nitric acid



Literature: Alpha radiolysis of nitric acid



Literature: Alpha radiolysis of nitric acid

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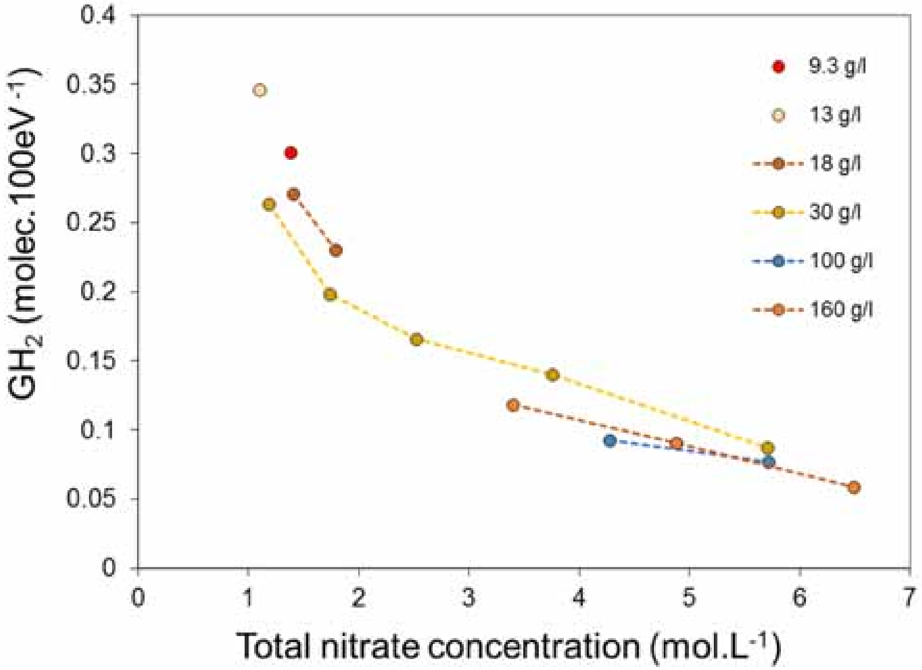
- Results for Pu fall below those for Cm and Po
- Kuno observed a small effect of Pu concentration on $G(H_2)$ but Bibler did not for addition of Pu to Cm solution



- Kuno saw an effect of solution depth while Bibler recorded an effect from solution agitation ($[NO_3^-]$ 0.7 – 10 mol.L^{-1})

Experimental method

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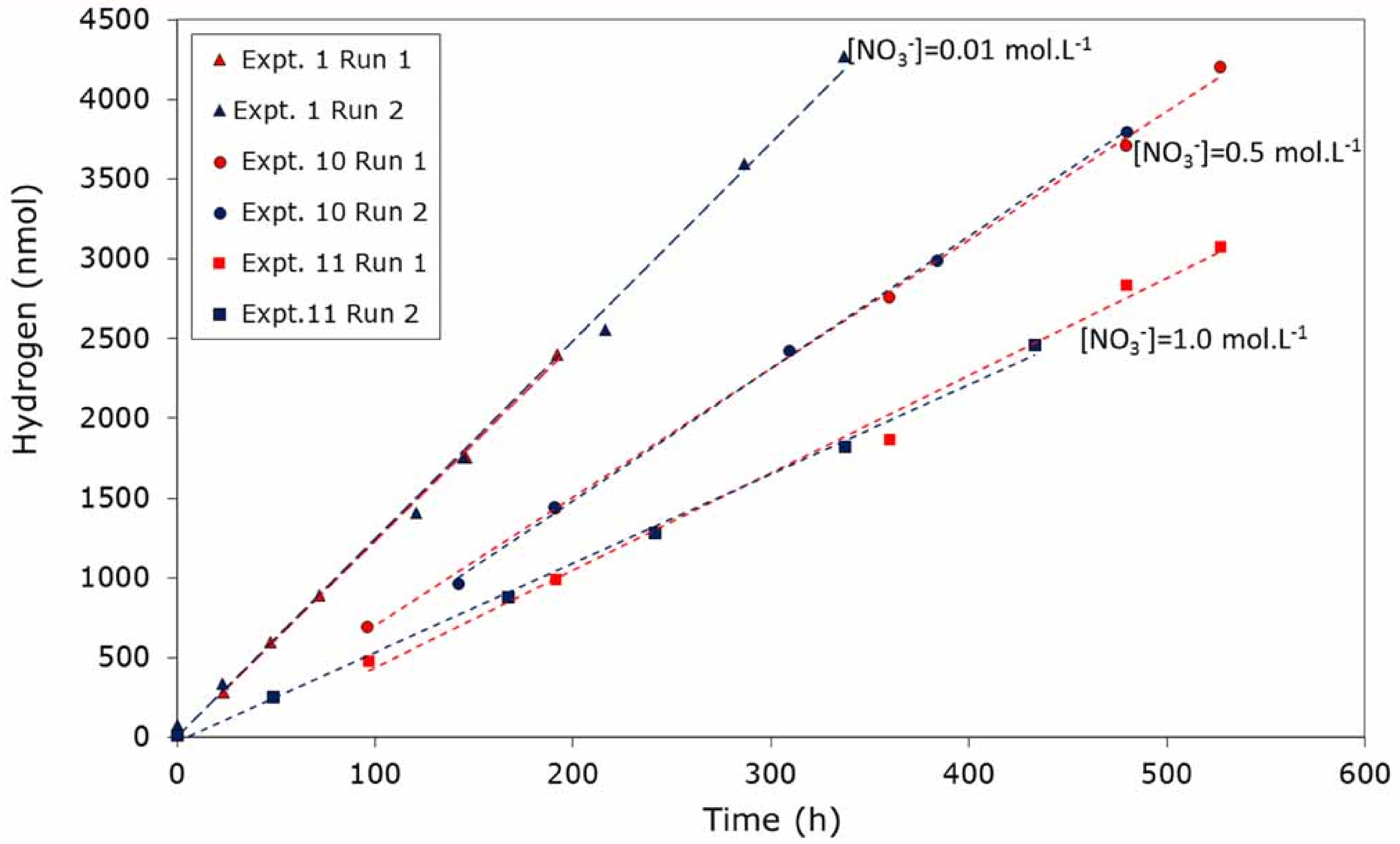
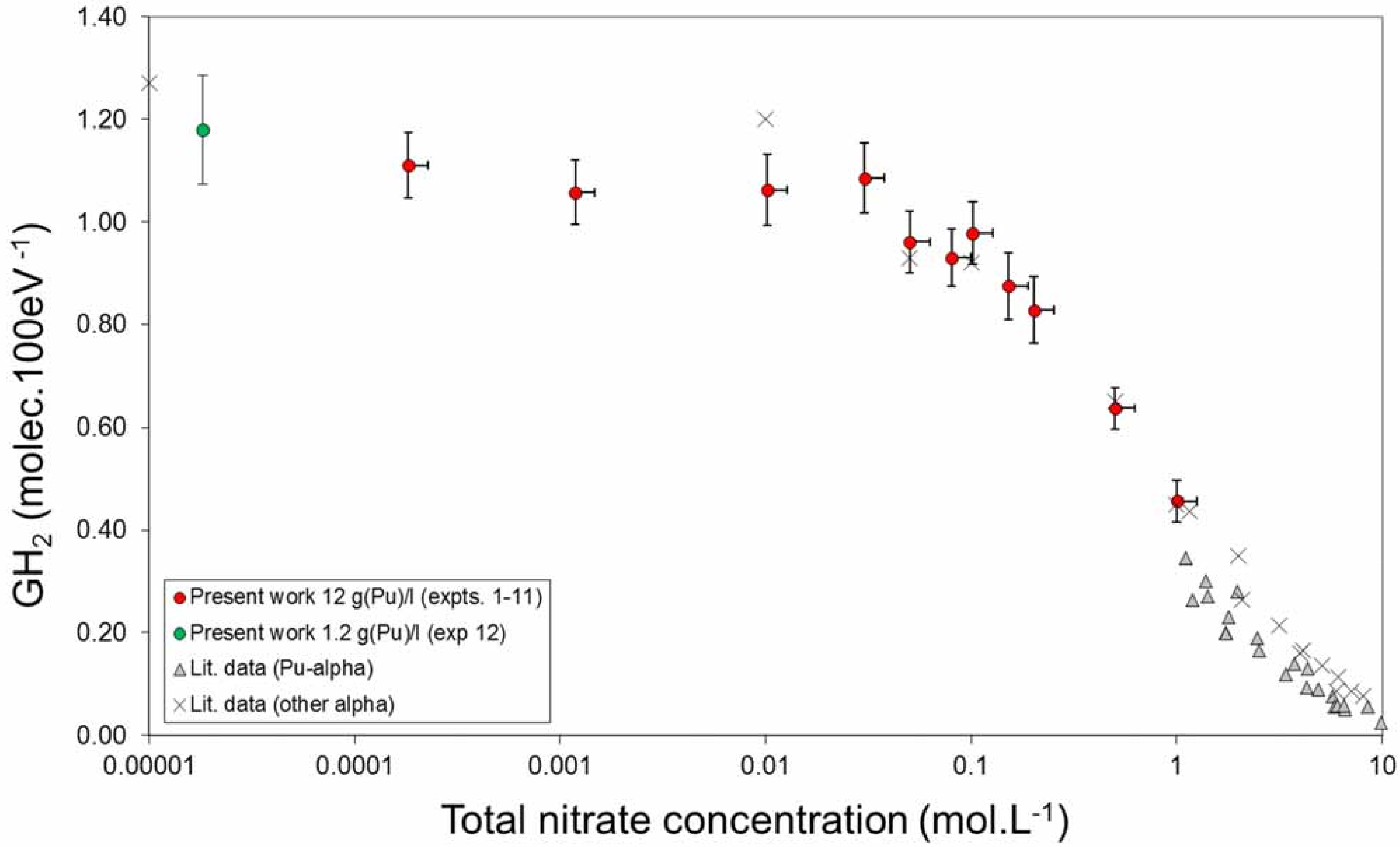
- Solutions
  - Pu concentration 12 g.L^{-1} (0.05 mol.L^{-1})
  - 0.75 mol.L^{-1} H_2SO_4
  - 0.0001-6 mol.L^{-1} HNO_3

- Hydrogen yield
  - Typically 0.5 ml solution in ~60 ml glass vessel
  - Vessel sealed and periodically headspace sampled by gas syringe (~10 ml gas) with stirring prior to sampling
  - Sampled gas volume replaced with air
  - Hydrogen concentration determined using µ-GC (Mol-sieve 5A column, Ar carrier, TCD detector)

Experimental method: Example hydrogen production rates



Initial results: plutonium nitrate



Effect of plutonium concentration?

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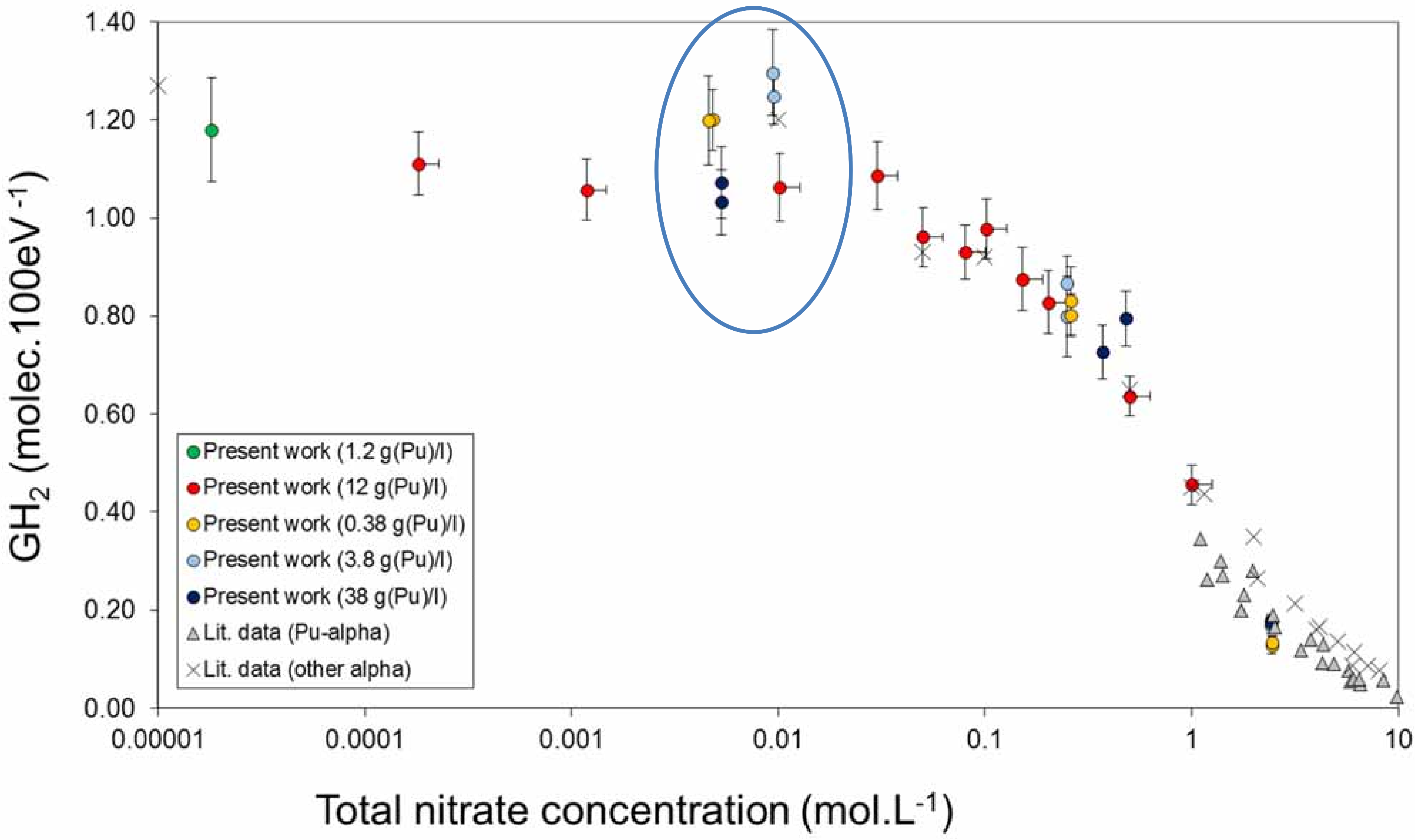
- Pu(IV) is a scavenger of hydrogen precursors
  - $Pu^{4+} + e^-_{aq} \rightarrow Pu^{3+}$ $k=3x10^{10}$ $L.mol^{-1}.s^{-1}$
- Analogous effect well established for Cu^{2+}
  - $Cu^{2+} + e^-_{aq} \rightarrow Cu^+$ $k=3.3x10^{10}$ $L.mol^{-1}.s^{-1}$
  - $Cu^{2+} + e^-_{pre} \rightarrow Cu^+$ $k \sim 1x10^{13}$ $L.mol^{-1}.s^{-1}$
- Compare with NO_3^-
  - $e^-_{aq} + NO_3^- \rightarrow NO_3^{2-}$ $k=9.7x10^9$ $L.mol^{-1}.s^{-1}$
  - $e^-_{pre} + NO_3^- \rightarrow NO_3^{2-}$ $k \sim 2x10^{13}$ $L.mol^{-1}.s^{-1}$
- Scavenging capacity = $k_S x[S]$
- Further experiments performed with a range of Pu concentration: 1-38 $g.L^{-1}$ (0.0004-0.16 $mol.L^{-1}$)

Pastina et al., *J. Phys. Chem. A*, 103 (1999) 5841

Results: Effect of plutonium concentration



Effect of plutonium concentration?

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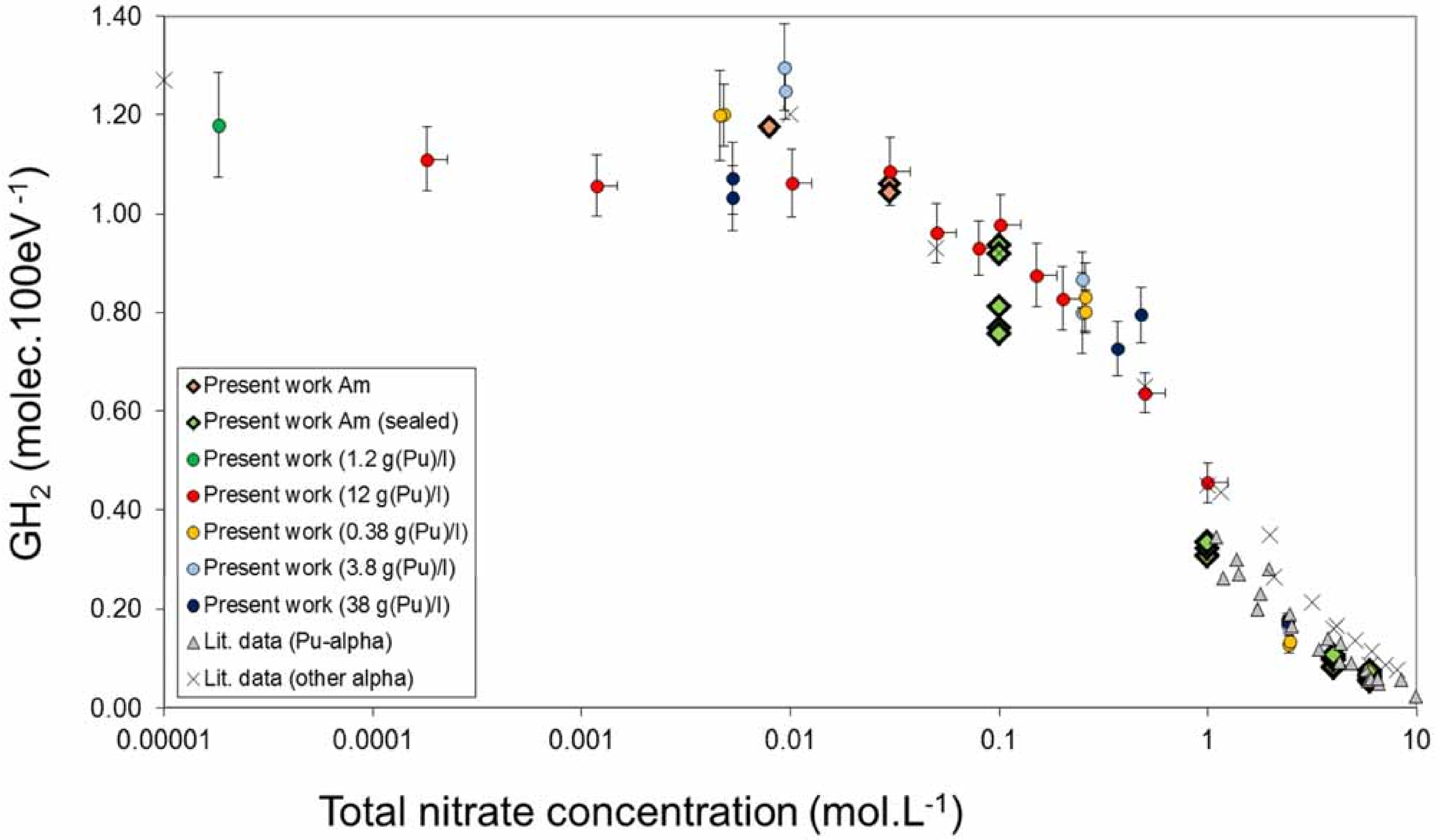
- Evidence of an effect from Pu concentration at low nitrate concentration
- Unlikely the concentration dependence seen by Kuno is due to Pu(IV) scavenging precursors of H_2
- Further measurement made using Am in nitric acid
- Am(III) does not scavenge precursors of hydrogen
- Two test methods used:
  - Same as previous method
  - Sealed “Single shot” vessels only sampled once but using 5 ml solution

Results: Americium nitric acid solutions



Conclusions/summary

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- New measurements of the molecular yield from nitric and sulphuric acid solutions reported, particularly at low concentrations of nitrate
- Results are consistent with previously reported data for alpha radiolysis at high nitrate concentrations
- Evidence of an effect of Pu concentration at low nitrate concentrations

Acknowledgements

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- SACSESS project

SACSESS
Safety of actinide separation processes

European Commission

EURATOM

- Sellafield Ltd.

- UK Nuclear Decommissioning Authority