Hydrogen Effects on Tritium Permeation Behavior at Low Partial Pressure

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**INL and STAR Facility**

- **Idaho National Laboratory (INL):**
  - Geographically, the largest lab in 10 multi-program US national laboratories
  - The nation’s lead laboratory for nuclear energy research and development
  - 52 reactors were designed and built in Idaho
  - The world’s first usable electricity from nuclear energy generated in EBR-I in 1951

- **Advanced Test Reactor (ATR)**
  - Light water moderated/cooled with Be neutron reflector
  - Max: 250 MW\textsubscript{th}, Four Leaf Clover” design
  - Materials and fuels testing, isotope production

- **Safety & Tritium Applied Research (STAR) Facility**
  - DOE less than Hazard Category 3 nuclear facility
  - Supports the mission of DOE SC Fusion Energy Sciences program (FES) and Nuclear Energy (NE)
  - Operates the Tritium Plasma Experiment (TPE)
  - Focuses on tritium retention and tritium permeation in fusion and fission materials
Outlines

• Motivation

• Theory

• Experiment

• Results and Discussion

• Conclusions and future work
Permeation behavior at low partial pressure
(mono-hydrogen component)

Mass Transport Properties:

- Solubility: \( K_s \)
- Diffusivity: \( D \)
- Dissociation rate constant: \( K_d \)
- Wall thickness: \( x \)
- Hydrogen partial pressure: \( p \)

“High” partial pressure:
- flux limited by bulk diffusion, \( \sim p^{0.5} \)

“Low” partial pressure:
- flux limited by surface dissociation/recombination, \( \sim p^1 \)

Transition is governed by the dimensionless number* \( W \):

\[
W = \frac{K_d x \sqrt{p}}{K_s D}
\]

\( W \ll 1 \quad \text{Surface Limited} \)
\( W \gg 1 \quad \text{Diffusion Limited} \)

\[
J = \frac{1}{2} K_d p \\
J = \frac{D K_s \sqrt{p}}{x}
\]

\(< 0.1 \text{ Pa}\)

References:
Typical condition in blanket (e.g KO TBS)

• Typical condition in H/D/T permeability literatures
  – Hydrogen (or deuterium) partial pressure: \( p_{H2}, p_{D2} \)
    • \( 10^3 < p_{H2}, p_{D2} \) [Pa] < \( 10^5 \)
  – Mono-hydrogen component permeation (\( H_2 \) or \( D_2 \)) system

• Condition in fusion blanket system
  – Hydrogen partial pressure: \( p_{H2} \)
    • \( p_{H2} \sim 10^2 \) Pa in the sweep gas (1000 ppm at STP)
  – Tritium partial pressure: \( p_{T2} \)
    • \( p_{T2} < 1 \) Pa in the sweep gas (< 10 ppm at STP)
  – Multi-hydrogen components permeation (\( H_2 \), \( T_2 \), HT) system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>FW heat flux</td>
<td>0.3 MW/m²</td>
</tr>
<tr>
<td>Neutron wall load</td>
<td>0.78 MW/m²</td>
</tr>
<tr>
<td>Thermal Power</td>
<td>0.98 MW</td>
</tr>
<tr>
<td>Structural material</td>
<td>KO-RAFM (ARAA) (&lt; 550 °C)</td>
</tr>
<tr>
<td>Breeder</td>
<td>( \text{Li}_2\text{TiO}_3 (&lt; 920 \text{ °C}) )</td>
</tr>
<tr>
<td></td>
<td>70% enrichment Li-6</td>
</tr>
<tr>
<td>Multiplier</td>
<td>Be (&lt; 650 °C)</td>
</tr>
<tr>
<td>Reflector</td>
<td>Graphite (&lt;1200 °C)</td>
</tr>
<tr>
<td>Size</td>
<td>1670(P) x 462(T) x 605(R) (mm)</td>
</tr>
<tr>
<td>Coolant</td>
<td>8 MPa He</td>
</tr>
<tr>
<td></td>
<td>1.14 kg/s (Nominal)</td>
</tr>
<tr>
<td></td>
<td>300 °C inlet / 500 °C outlet</td>
</tr>
<tr>
<td>Purge gas</td>
<td>He with 0.1 % ( \text{H}_2 )</td>
</tr>
<tr>
<td>TBM-shield</td>
<td>316L(N)-IG Block/Cooling Channels</td>
</tr>
<tr>
<td></td>
<td>ITER FW/BLK-PHTS (40 °C, 4 MPa)</td>
</tr>
</tbody>
</table>
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Thermodynamic equilibriums in multi-components (H₂, T₂, HT) system

- Consider three thermodynamic equilibriums
  1) Gas phase equilibrium between H₂, T₂ and HT
  2) Surface equilibrium between H₂ molecule and dissolved H atom
  3) Surface equilibrium between T₂ molecule and dissolved T atom

\[(1)\quad H_2 + T_2 \leftrightarrow 2HT\quad K_{HT} = \frac{p_{HT}^2}{p_{HH} p_{TT}} = \frac{x_{HT}^2}{x_{HH} x_{TT}}\]

\[(2)\quad H_2 \leftrightarrow 2H\quad c_H = K_H \sqrt{p_{HH}} = \sqrt{x_{HH}} K_H \sqrt{p_{total}}\]

\[(3)\quad T_2 \leftrightarrow 2T\quad c_T = K_T \sqrt{p_{TT}} = \sqrt{x_{TT}} K_T \sqrt{p_{total}}\]

**NOTE:** \(p_{HH}, p_{TT}, p_{HT}\) are partial pressures of H₂, T₂, and HT, respectively.

- Formation of HT molecules reduces the partial pressures of H₂ and T₂
- Surface equilibrium between HT molecules and dissolved H and T atoms in the metal was included/implied by the gas phase equilibrium.

Equilibrium constant for the reaction \( \text{H}_2 + \text{T}_2 \leftrightarrow 2\text{HT} \)

- Fitted the experimental data (W.M. Jones, *J. Chem. Phys.* 16 (1948) 1077) with
  \[ \log_{10} K_{eq} = A + B \log_{10} T + C T^{-1} \]
- Obtained the best fit with non-linear least square fitting
  \[ \log_{10} K_{eq} = (0.922275) + (-0.083398) \log_{10} T + (-91.47218) T^{-1} \]

\[ \text{H}_2 + \text{T}_2 \leftrightarrow 2\text{HT} \]

\[ K_{HT} = \frac{p_{HT}^2}{p_{HH} p_{TT}} = \frac{x_{HT}^2}{x_{HH} x_{TT}} \]

T permeability in high H$_2$ partial pressure

- For $p_{HH}^1 = p_{HH}^2$ condition:
  - Only tritium diffusion is considered.

- Consider 1D diffusion equation of tritium

\[
J_D^T = \frac{D_T K_T A}{\Delta x} \left( \sqrt{p_{TT}^1} - \sqrt{p_{TT}^2} \right) \approx \frac{D_T K_T A}{\Delta x} \left( \sqrt{p_{TT}^1} \right)
\]

\[
p_{TT}^1 = \frac{(p_{HT}^1)^2}{K_{HT}^1 p_{HH}^1}
\]

\[
J_D^T \approx \frac{D_T K_T A}{\Delta x \sqrt{K_{HT}^1}} \frac{p_{HT}^1}{\sqrt{p_{HH}^1}} \propto \frac{p_{HT}^1}{\sqrt{p_{HH}^1}}
\]

\[
P_T = D_T K_T \approx \frac{J_D^T \Delta x}{A} \sqrt{K_{HT}^1} \frac{\sqrt{p_{HH}^1}}{p_{HT}^1}
\]

Reference: J.T. Bell and J.D. Redman, J. Phys. Chem. 82 (1978) 2834
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Tritium gas absorption and permeation

- Is a unique tritium permeation experiment dedicated to
  - measure tritium transport properties (e.g. diffusivity, solubility, and permeability) in liquid (e.g. PbLi) and disc shaped metal specimens at realistic fusion sweep gas conditions at temperature up to < 700 C
  - low tritium partial pressure 0.01-10 Pa (0.1-100 ppm)
  - hydrogen partial pressures 10-1000 Pa, (100-10000 ppm)
  - Capable of handling radioactive materials

- Utilizes Ventilated enclosure for tritium containment

Fig. 1. Simplified schematic of the tritium permeation measurement system.

Ref: R.J. Pawelko et.al., *JNM* 102 (2016)
Photos of TGAP test section

• KO NRFI-UCLA-INL Phase I (July 2013 – July 2016)
  – Measure tritium permeation rate from KO RAFM ARAA material
  – Plan to measure tritium permeation from neutron-irradiated RAFM ARAA material in Phase II
Tritium Supply System (TSS) for < 1 Pa HT source

- Is a new tritium supply system for TGAP experiment
  - Capable of varying \( T_2 \) concentration by a factor 250 with const. \( H_2/He \)
  - 1\(^{st} \) (2\(^{nd} \)) mixing:
    - 0.2 Ci (5.0 Ci) of tritium was transferred to TSS system
    - Pressurized with 1000 ppm \( H_2/He \) up to 285 psig (~ 19.6 atm)
    - Calculated \( T_2 \) concentration was 2.3 (56.9) ppm HT / 1000 ppm \( H_2/He \)

- Utilizes Laboratory hood for tritium containment

### TSS gas mixture calculations _28MAR16_

<table>
<thead>
<tr>
<th>Date</th>
<th>Volume (cc)</th>
<th>( T_2 ) activity (Ci)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>28-Sep-11</td>
<td>11.35</td>
<td>0.209</td>
<td>Loaded</td>
</tr>
<tr>
<td>28-Mar-16</td>
<td>11.35</td>
<td>0.209</td>
<td>Decay corr.</td>
</tr>
</tbody>
</table>

Given:

- TSS internal volume: 3.7702 liter (304L-HDF8-1GAL)
- \( T_2 \) in 11.35 cc transfer volume: 0.209 Ci or 3.60E-06 moles
  1 mole \( T_2 \) contains: 58023 Ci
  1 mole HT contains: 29011.5 Ci or 7.20E-06 moles

**NOTE:** Majority of \( T_2 \) were converted into HT once mixed with 1000 ppm \( H_2/He \) gas

\[ R = 0.0821 \text{ liter-atm/mole} - K \]

- Room temperature: 295 K = 71.3 °F
- Standard atmospheric pressure: 760 torr = 14.7 psi
- \( T_2 \) transferred to 3.7702 liter TSS cylinder: 0.208 Ci or 7.18E-06 moles

### 3.7702 liter TSS cylinder manifold

<table>
<thead>
<tr>
<th>(psia)</th>
<th>(Total moles)</th>
<th>(HT ppm)</th>
<th>(HT torr)</th>
<th>(HT Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.0</td>
<td>3.18</td>
<td>2.3</td>
<td>0.04</td>
<td>4.67</td>
</tr>
</tbody>
</table>

Expected pC response at 1e5 Pa: 2.69 Ci/m^3
Tritium permeation in KO RAFM

- Tritium – (1000 ppm) hydrogen – helium gas from TSS
  - Newly constructed TSS provided:
    - Similar hydrogen concentration in primary and secondary, and avoided counter permeation of hydrogen \( p_{H2}^1 = p_{H2}^2 \)
    - Capability to change tritium concentration by a factor of 250
  - Ion chamber provides \( J_D^T \) and \( p_{HT} \) since \( p_{H2} >> p_{HT} >> p_{T2} \)
  - Then tritium partial pressure can be calculated for \( H_2 + T_2 \leftrightarrow 2HT \)
    - \( p_{T2} = p_{HT}^2 / (K_{HT} * p_{H2}) \)

- Experimental conditions:
  - Material: 20 mm OD Advanced Reduced Activation Alloy (ARAA)
  - Thickness: 0.5, 1.0, and 2.0 mm
  - Temperature: 400(± 5), 450(± 5), and 500(± 5) °C
  - Primary gas: (\(10^{-3} – 10^{-1}\) Pa) \( T_2 \) – (99Pa) \( H_2 \) – He at total pres. of \(10^5\) Pa
  - Primary flow rate: 50(± 1) sccm
  - Secondary gas: (97Pa) \( H_2 \) – He at total pres. of \(10^5\) Pa
  - Secondary flow rate: 200(± 2) sccm
T permeability can be measured in multi-components (H₂, T₂, HT) system

• Known parameters:
  – Δx  Sample thickness [m]
  – A   Surface area [m²]
  – $K_{HT}$  Equilibrium constant for $H_2 + T_2 = 2HT$ [ND]
  – $p_{HH}$  $H_2$ partial pressure [Pa]

$$P_T = D_T K_T \approx \frac{J_D^T \Delta x \sqrt{K_{HT}}}{A} \frac{\sqrt{p_{HH}}}{\rho_{HT}}$$

• Experimentally measured values:
  – $J_D^T$  Tritium (HT) permeation rate [mole/sec]
  – $p_{HT}$  HT partial pressure [Pa]
Ion chamber response on different gas

- Typical issues in ion chamber measurement
  - Ion chamber cannot distinguish flowing tritium species (T\(_2\) or HT)
  - Ion chamber needs a trace amount of (> 0.01 %) H\(_2\) in sweep gas (He or Ar), and its response (ion saturation current) is gas dependent.

Fig. 3. Change in normalized tritium release rate, \(R/R_0\), with elapsed time, \(t\), in the case of He or He–1% H\(_2\) sweep gas.

**NOTE:** H\(_2\) partial pressures must be constant in primary and secondary.

Reference:
Measurement of $J_D^T$ and $p_{HT}$

- Solutions in ion chamber measurement
  - $p_{H2} >> p_{T2}$ and $p_{H2}^1 = p_{H2}^2$ eliminated the above two issues.

- Measurement of $J_D^T$ and $p_{HT}$
  - $J_D^T$ Tritium permeation rate [mole/sec]
    - When $p_{H2} >> p_{T2}$ condition, ion chamber in the secondary (pIC) can provide tritium (HT) permeation rate [mole/sec]

  - $p_{HT}$ HT partial pressure [Pa]
    - When $p_{H2} >> p_{T2}$ condition, ion chamber in the primary (pIC) can provide HT partial pressure [Pa]
Partial pressures of $p_{H2}$, $p_{HT}$, $p_{T2}$

**NOTE:**

- We can assume $p_{HT} \gg p_{T2}$ in the low $p_{T2}$ condition ($p_{T2} \ [Pa] < 1$)
- $T_2$ partial pressure follows a square of HT partial pressure ($p_{T2} \sim p_{HT}^2$) dependence
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Hydrogen isotope partial pressure dependence on tritium permeation

\[ \frac{J_D^T \Delta x}{A} \approx D_T K^T \left( \frac{p^{1}_{HT}}{\sqrt{K^T}} \frac{1}{\sqrt{p^{1}_{HH}}} \right) = D_T K^T \sqrt{p^{1}_{TT}} \]

\[ p^{1}_{HT}, p^{1}_{TT} \]
Tritium permeability in RAFM

\[ P_T = D_T K_T \approx \frac{J_D^T \Delta x \sqrt{K_{HT}}}{A} \frac{\sqrt{p_{HH}}}{p_{HT}} \]

\( T \) permeability in ARAA
\( P_T = P_0 \exp(-E_p / kT) \)
\( P_0 = 9.8 \times 10^{-8} \text{ [mol m}^{-1}\text{s}^{-1}\text{Pa}^{-0.5}] \)
\( E_p = 47.8 \text{ [kJ/mol]} \)

NOTE: All the D permeability data of literature were adjusted for T by sqrt (mass2/mass3).
Outline of the talk

• Motivation

• Theory

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• Results and Discussion

• Summary and future work
Summary and future work (1/2)

• At realistic blanket T condition ($p_{H2} >> p_{HT} >> p_{T2}$)
  - Tritium permeation behavior follows linear dependence to $p_{HT}$
  - Gas phase equilibrium is important to understand kinetics in multi-hydrogen components permeation ($H_2$, $T_2$, HT) system
  - Formation of HT molecules reduces the partial pressures of $H_2$ and $T_2$
  - $T_2$ partial pressure follows a square of HT partial pressure ($p_{T2} \sim p_{HT}^2$) dependence. Therefore, tritium (HT) permeation flux appears to follow a linear dependence of HT partial pressure even though it is in diffusion-limited permeation.

• Tritium permeability measurement at low $p_{HT}$ and $p_{T2}$
  - We have demonstrated (revived) tritium permeability measurement method at low $p_{HT}$ and $p_{T2}$, and high $p_{H2}$
  - Gas phase equilibrium is important to obtain tritium permeability in multi-hydrogen components permeation ($H_2$, $T_2$, HT) system
  - Measured T permeability in KO RAFM agrees with other literature data from RAFM.
Summary and future work (2/2)

• Hydrogen effects in tritium permeation at low $p_{HT}$ and $p_{T2}$
  – Will have profound effects on tritium permeation, reducing tritium permeation rate by > 2 orders of magnitudes.
  – Although this mechanism applies to non-hydride forming metal (e.g. steel, nickel alloy, refractory metal), experimental validation with other fusion material at low $p_{HT}$ and $p_{T2}$ is required to confirm this significant tritium permeation reduction in fusion materials.
  – Can enhance the operational safety in fusion blanket system.

• Future work
  – Continue investigating tritium permeation at low partial pressure on the following materials:
    • ARAA samples (0.5, 1.0 and 2.0 mm) under NFRI-UCLA-INL Phase I
    • Tungsten under US-Japan PHENIX
  – Improve efficiency of low level tritium counting:
    • Procure on-line liquiec scintillation counter (e.g. LabLogic Beta-RAM etc.)
  – Improve understanding of ion chamber in gas mixture:
    • Perform numerical modeling/simulation to predict ion chamber response