Permeation of multiple isotopes in the transition between surface- and diffusion-limited regimes

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Overview

- At high pressure, tritium permeation is diffusion-limited
- At low pressure, it may become surface-limited
  - What is the transition pressure?
- If other isotopes are present, how does that affect:
  - The diffusion-limited regime?
  - The surface-limited regime?
  - The transition region?
  - The transition point?
- Real fusion environments have multiple isotopes at low partial pressures, so these things need to be understood
- The analysis presented here should prove useful for the design and interpretation of experiments
Fundamental Processes

- Dissociation: \( J_{d,1} = \frac{1}{2} K_d P \)
- Recombination: \( J_{r,i} = \frac{1}{2} K_r C_i^2 \)
- Diffusion: \( J = \frac{-D(C_2-C_1)}{x} \)
One isotope, diffusion-limited, $P_2 = 0$

Say the dissociation and recombination processes are equal (i.e., much faster than diffusion):

$$K_d P = K_r C_1^2$$

This gives Sieverts’ Law:

$$C_1 = K_s \sqrt{P}$$

Where the solubility is defined by:

$$K_s = \sqrt{\frac{K_d}{K_r}}$$

And the diffusion-limited flux is:

$$J_{DL} = \frac{DK_s \sqrt{P}}{x}$$
One isotope, surface-limited, $P_2 = 0$

If diffusion is much faster than dissociation and recombination, the concentration profile is flat:

$$C_1 = C_2$$

The recombination rates must be equal:

$$J_{r,2} = J_{r,1} = J_r$$

A flux balance gives

$$J_{d,1} = 2J_r$$

So the surface-limited flux is:

$$J_{SL} = \frac{1}{2}K_dP$$
One isotope, all regimes, $P_2=0$

- A general flux balance at each surface gives

$$K_dP - K_rC_1^2 = \frac{-D(C_2-C_1)}{x}$$

$$\frac{-D(C_2-C_1)}{x} = K_rC_2^2$$

- Divide by the diffusion-limited flux $J_{DL} = \frac{DK_s\sqrt{P}}{x}$ to get a dimensionless equation:

$$W \left(1 - v^2\right) = v - u$$

$$v - u = Wu^2$$

- Where $u, v$ are the dimensionless concentrations

$$u = \frac{C_2}{K_s\sqrt{P}} \quad v = \frac{C_1}{K_s\sqrt{P}}$$

- And the parameter $W = \frac{K_d\sqrt{P}}{DK_s}$ has a special meaning…

One isotope, all regimes, $P_2=0$

- The dimensionless equations can be rearranged as follows:

$$v = \sqrt{1 - u^2} \quad W^2 u^4 + 2W u^3 + 2u^2 = 1$$

- Taking the limit $W \to 0$ in the above gives the surface-limited case:

$$J_{SL} = \frac{1}{2} K_d P \quad C_1 = C_2 = K_s \sqrt{\frac{P}{2}}$$

- Taking the limit $W \to \infty$ gives the diffusion-limited case:

$$J_{DL} = \frac{DK_s \sqrt{P}}{x} \quad C_1 = K_s \sqrt{P} \quad C_2 = 0$$

$W$ is a dimensionless permeation number that governs the transition between regimes, with the center of the transition region in the vicinity of $W \sim 1$

- The “low” pressure required for surface limiting is $P \ll \left( \frac{DK_s}{K_d x} \right)^2$

Multiple isotopes

H and T behavior is coupled through this term

- **Dissociation:**
  \[ J_{d,H_2,i} = \frac{1}{2} K_d P_{H_2,i} \]
  \[ J_{d,T_2,i} = \frac{1}{2} K_d P_{T_2,i} \]
  \[ J_{d,HT,i} = \frac{1}{2} K_d P_{HT,i} \]

- **Recombination:**
  \[ J_{r,H_2,i} = \frac{1}{2} K_r C_{H,i}^2 \]
  \[ J_{r,T_2,i} = \frac{1}{2} K_r C_{T,i}^2 \]
  \[ J_{r,HT,i} = K_r C_{H,i} C_{T,i} \]

- **Diffusion:**
  \[ J_H = \frac{-D_H(C_{H,2} - C_{H,1})}{x} \]
  \[ J_T = \frac{-D_T(C_{T,2} - C_{T,1})}{x} \]

Side 1: highest partial pressure (sum of all isotopes)
Flux balance for multiple isotopes

• Define “effective” pressures:
  \[ P_T \equiv P_{T_2} + \frac{1}{2} P_{HT} \quad P_H \equiv P_{H_2} + \frac{1}{2} P_{HT} \]

• Tritium flux:
  \[ K_d P_{T,1} - K_r C_{T,1}^2 - K_r C_{T,1} C_{H,1} = \frac{D_T (C_{T,1} - C_{T,2})}{x} \]
  \[ \frac{D_T (C_{T,1} - C_{T,2})}{x} = K_r C_{T,2}^2 + K_r C_{T,2} C_{H,2} - K_d P_{T,2} \]

• Hydrogen flux:
  \[ K_d P_{H,1} - K_r C_{H,1}^2 - K_r C_{T,1} C_{H,1} = \frac{D_H (C_{H,1} - C_{H,2})}{x} \]
  \[ \frac{D_H (C_{H,1} - C_{H,2})}{x} = K_r C_{H,2}^2 + K_r C_{T,2} C_{H,2} - K_d P_{H,2} \]

• Non-dimensionalize by a factor \( J_\infty = D_T K_s \sqrt{P_{T,1} + P_{H,1}/x} \) and define:

  • Dimensionless concentrations:
    \[ u_T = \frac{C_{T,2}}{K_s \sqrt{P_{T,1} + P_{H,1}}} \quad v_T = \frac{C_{T,1}}{K_s \sqrt{P_{T,1} + P_{H,1}}} \]
    \[ u_H = \frac{C_{H,2}}{K_s \sqrt{P_{T,1} + P_{H,1}}} \quad v_H = \frac{C_{H,1}}{K_s \sqrt{P_{T,1} + P_{H,1}}} \]

  • Generalized dimensionless permeation number:
    \[ W = \frac{K_d x \sqrt{P_{T,1} + P_{H,1}}}{K_s D_T} \]
General Equations

\[
W \left( \frac{P_{T,1}}{P_{T,1}+P_{H,1}} - v_{T}^2 - v_{T}v_{H} \right) = v_{T} - u_{T}
\]
\[
v_{T} - u_{T} = W \left( u_{T}^2 + u_{T}u_{H} - \frac{P_{T,2}}{P_{T,1}+P_{H,1}} \right)
\]

\[
W \left( \frac{P_{H,1}}{P_{T,1}+P_{H,1}} - v_{H}^2 - v_{T}v_{H} \right) = \left( \frac{D_{H}}{D_{T}} \right) (v_{H} - u_{H})
\]
\[
\left( \frac{D_{H}}{D_{T}} \right) (v_{H} - u_{H}) = W \left( u_{H}^2 + u_{T}u_{H} - \frac{P_{H,2}}{P_{T,1}+P_{H,1}} \right)
\]

- The above describe transport of both isotopes, in any configuration, and in all transport regimes.
- Form of equations indicates that the concepts “surface-limited” and “diffusion-limited” apply only to the sum of all isotopes.
- We can identify these by taking limits of \( W \)!
Two isotopes, diffusion-limit

- In the limit $W \rightarrow \infty$:

$$C_{T,1} = \frac{K_s P_{T,1}}{\sqrt{P_{T,1}+P_{H,1}}}$$

$$C_{T,2} = \frac{K_s P_{T,2}}{\sqrt{P_{T,2}+P_{H,2}}}$$

$$C_{H,1} = \frac{K_s P_{H,1}}{\sqrt{P_{T,1}+P_{H,1}}}$$

$$C_{H,2} = \frac{K_s P_{H,2}}{\sqrt{P_{T,2}+P_{H,2}}}$$

$$J_T = \frac{D_T K_s}{x} \left( \frac{P_{T,1}}{\sqrt{P_{T,1}+P_{H,1}}} - \frac{P_{T,2}}{\sqrt{P_{T,2}+P_{H,2}}} \right)$$

$$J_H = \frac{D_H K_s}{x} \left( \frac{P_{T,1}}{\sqrt{P_{T,1}+P_{H,1}}} - \frac{P_{T,2}}{\sqrt{P_{T,2}+P_{H,2}}} \right)$$

- Flux measurements in this limit identify the permeability $D_T K_s$

- In general (especially in “counter-permeation”) the pressures of all isotopes on both sides of the membrane must be measured!
Two isotopes, surface-limit

• In the limit $W \to 0$:

\[
C_{T,1} = C_{T,2} = \frac{K_s (P_{T,1} + P_{T,2})}{\sqrt{2(P_{T,1} + P_{H,1} + P_{T,2} + P_{H,2})}} \quad J_T = \frac{1}{2} K_d (P_{T,1} - P_{T,2})
\]

\[
C_{H,1} = C_{H,2} = \frac{K_s (P_{H,1} + P_{H,2})}{\sqrt{2(P_{T,1} + P_{H,1} + P_{T,2} + P_{H,2})}} \quad J_H = \frac{1}{2} K_d (P_{H,1} - P_{H,2})
\]

• Flux measurements in this limit identify the dissociation rate constant $K_d$
• And by extension, the recombination rate constant $K_r$
• Note that the presence of a second isotope does not change the flux of the first in the surface limit
• But it does change the concentration in the solid membrane!
• The “low” pressure required for surface limiting is $P_{T,1} + P_{H,1} \ll \left( \frac{D_T K_s}{K_d x} \right)^2$
Co-permeation: three regimes

- Consider a “co-permeation” experiment in which downstream pressures are maintained near zero

- In the surface limit: \( J_T = \frac{1}{2} K_d P_{T,1} \)

- In the diffusion limit, with \( P_{T,1} \gg P_{H,1} \): \( J_T = \frac{D_T K_s \sqrt{P_{T,1}}}{x} \)

- In the diffusion limit, with \( P_{T,1} \ll P_{H,1} \): \( J_T = \frac{D_T K_s P_{T,1}}{x \sqrt{P_{H,1}}} \)

- This last case is diffusion-limited, but has a linear dependence on the tritium pressure!
- Refer to this as “isotope-limited”
Co-permeation examples

• Even a small amount of hydrogen (e.g. impurity levels) can matter
• The “isotope-limited” slope is easily mistaken for the surface limited slope
Conclusions

• A system of equations describing permeation of multiple isotopes across all transport regimes has been presented.

• A generalized permeation number has been shown to govern the transition from surface- to diffusion-limited permeation, concepts that apply to the sum of all isotope pressures.

• In general it is necessary to measure all pressures of all isotopes to adequately characterize a permeation experiment—especially for the case of “counter-permeation”.

• At low tritium pressures, hydrogen may impose an “isotope-limited” regime that resembles the surface limit, but has a different slope unrelated to the dissociation rate constant.
  – Even impurity-level concentrations of hydrogen might cause this.

• Provided all isotope pressures are measured, the expressions here provide the appropriate framework for parameter estimation in such experiments.