

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

Paul W. Humrickhouse

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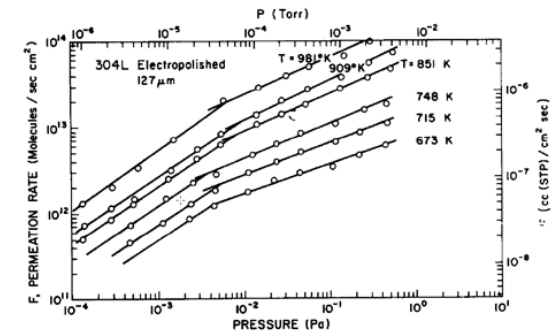


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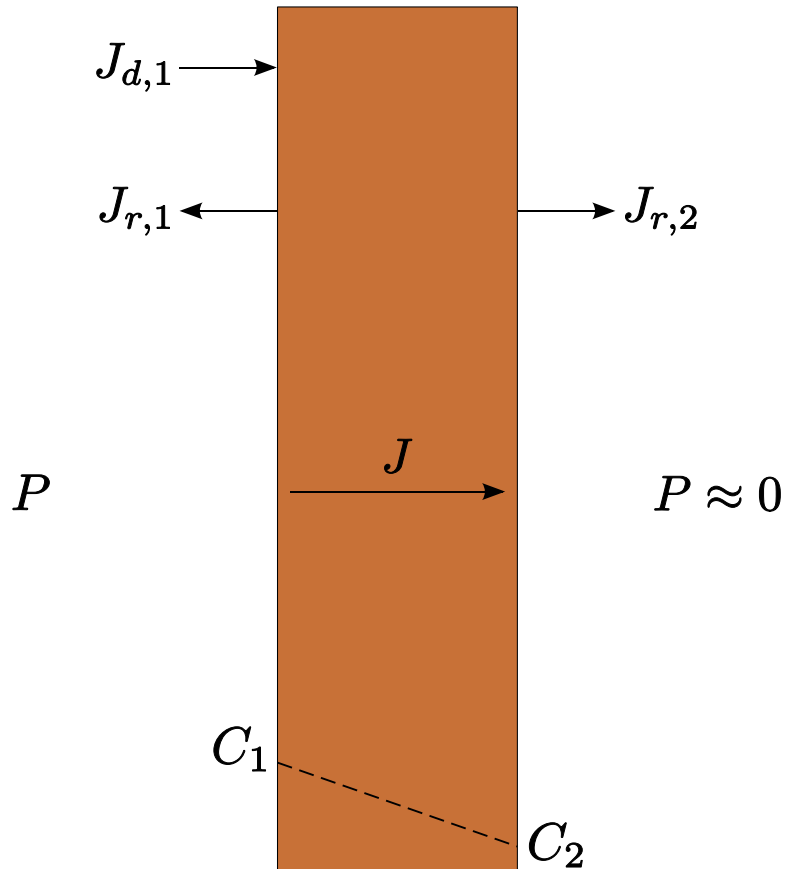
Overview

- 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



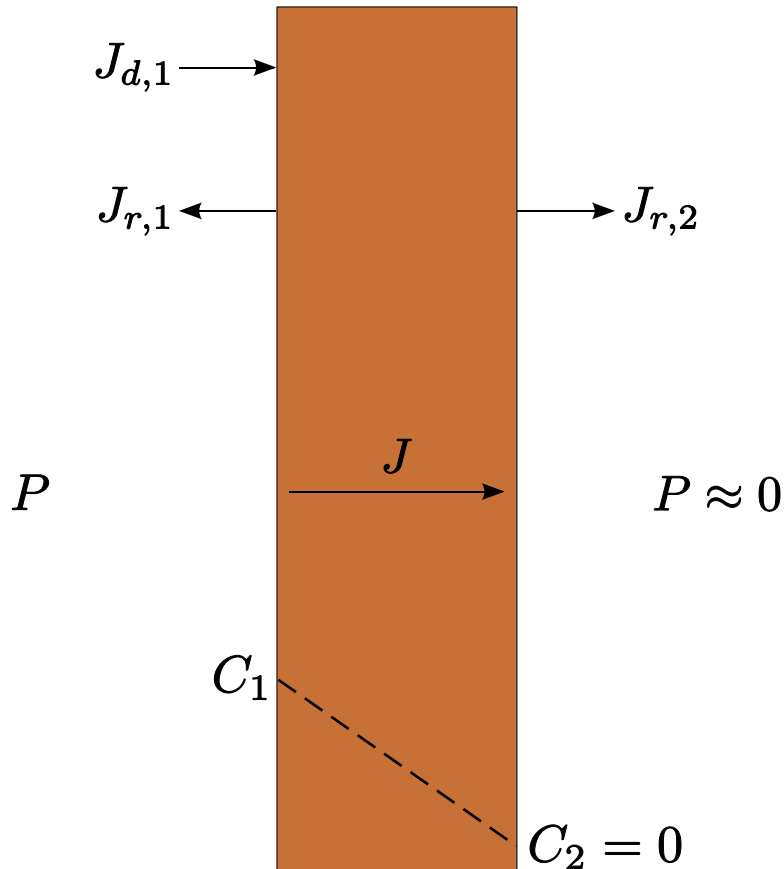
Perkins and Noda *JNM* 71 (1978) 349-364.

Fundamental Processes



- Dissociation: $J_{d,1} = \frac{1}{2}K_dP$
- Recombination: $J_{r,i} = \frac{1}{2}K_rC_i^2$
- 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:

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

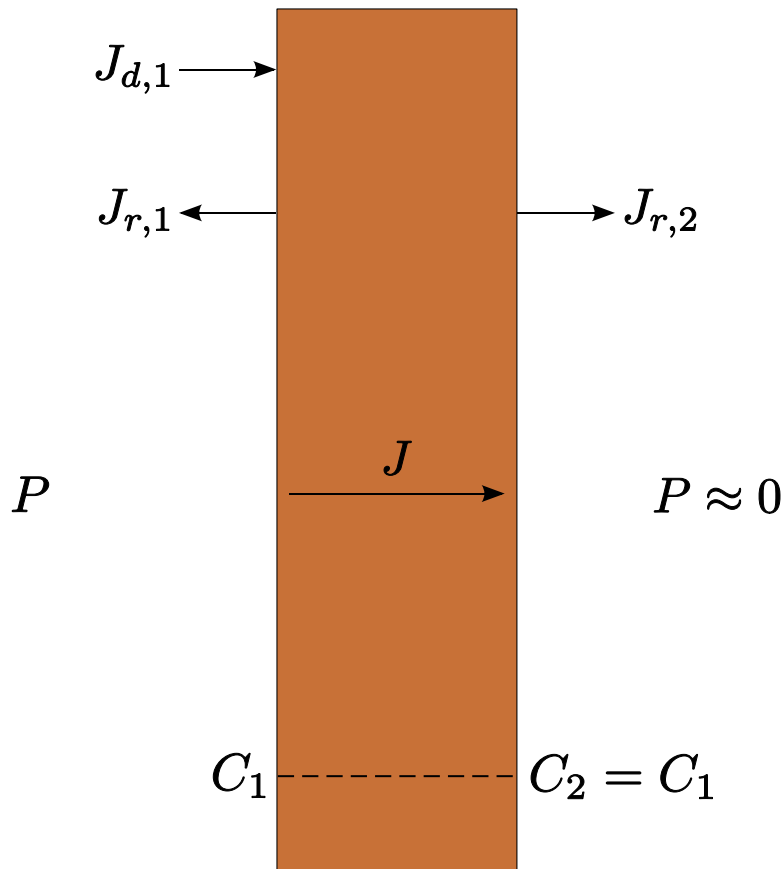
- Where the solubility is defined by:

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

- 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

$$K_d P - K_r C_1^2 = \frac{-D(C_2 - C_1)}{x}$$

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

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

$$W(1 - v^2) = v - u$$

$$v - u = Wu^2$$

- 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 $W = \frac{K_d x \sqrt{P}}{DK_s}$ 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 $W \rightarrow 0$ in the above gives the surface-limited case:

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

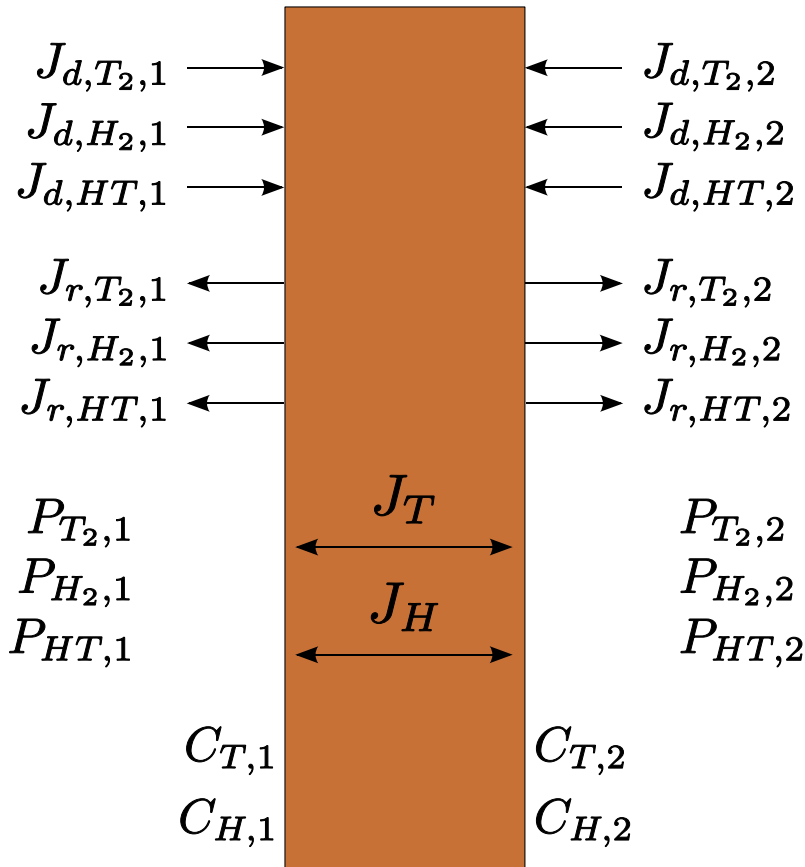
- Taking the limit $W \rightarrow \infty$ gives the diffusion-limited case:

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

- 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: $P_T \equiv P_{T_2} + \frac{1}{2}P_{HT}$ $P_H \equiv P_{H_2} + \frac{1}{2}P_{HT}$

- 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 $W \rightarrow \infty$:

$$\begin{aligned}
 C_{T,1} &= \frac{K_s P_{T,1}}{\sqrt{P_{T,1} + P_{H,1}}} & J_T &= \frac{D_T K_s}{x} \left(\frac{P_{T,1}}{\sqrt{P_{T,1} + P_{H,1}}} - \frac{P_{T,2}}{\sqrt{P_{T,2} + P_{H,2}}} \right) \\
 C_{T,2} &= \frac{K_s P_{T,2}}{\sqrt{P_{T,2} + P_{H,2}}} \\
 C_{H,1} &= \frac{K_s P_{H,1}}{\sqrt{P_{T,1} + P_{H,1}}} & J_H &= \frac{D_H K_s}{x} \left(\frac{P_{T,1}}{\sqrt{P_{T,1} + P_{H,1}}} - \frac{P_{T,2}}{\sqrt{P_{T,2} + P_{H,2}}} \right) \\
 C_{H,2} &= \frac{K_s P_{H,2}}{\sqrt{P_{T,2} + P_{H,2}}}
 \end{aligned}$$

- 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 $W \rightarrow 0$:

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

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

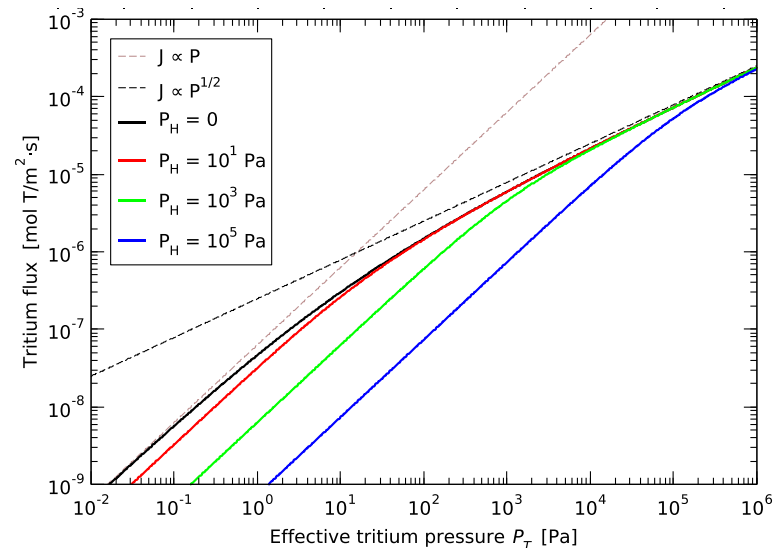
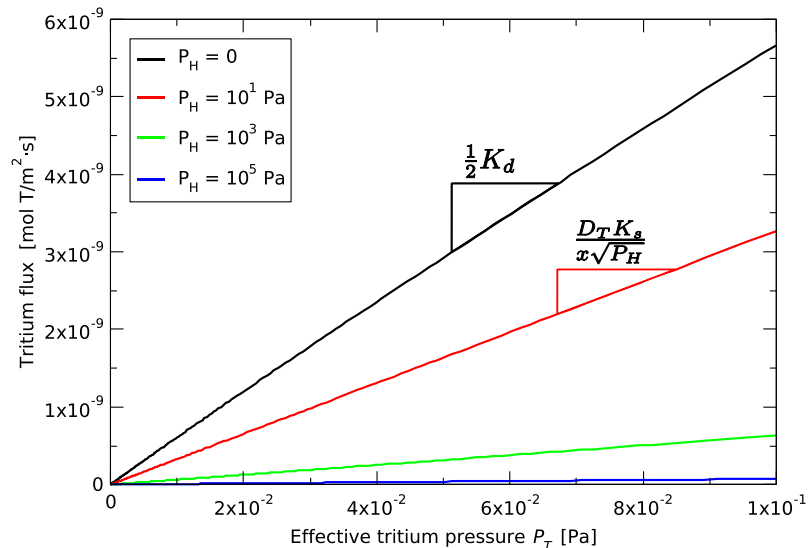
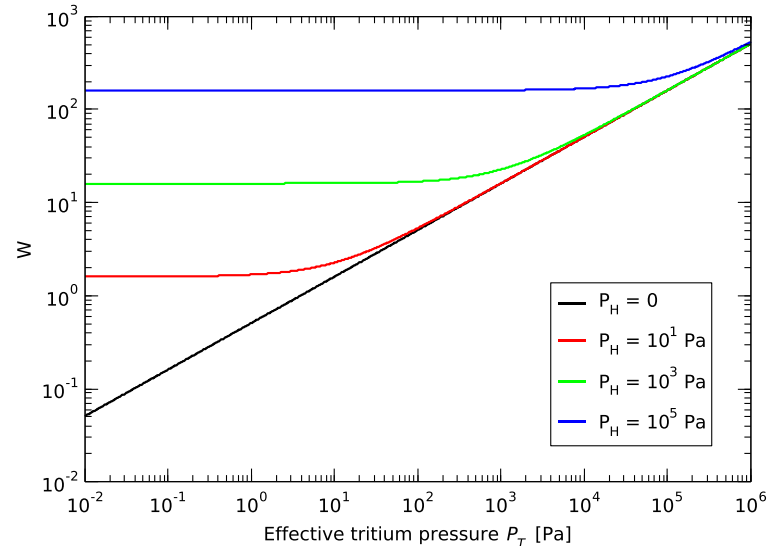
- Flux measurements in this limit identify the *dissociation rate constant* K_d
- And by extension, the *recombination rate constant* K_r
- Note that the presence of a second isotope does *not* change the flux of the first in the surface limit
- But it *does* change the concentration in the solid membrane!
- 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