Hydrogen Fuel Cells

Modeling and Computations

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Acknowledgment

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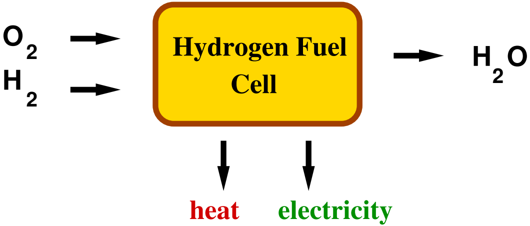
http://powerandenergy.com

Overview of the talk

- The workings of a hydrogen fuel cell
- A mathematical model for hydrogen-palladium interaction
- Two mathematical problems:
  - Solution and analysis of an ODE
  - Solution and analysis of a PDE

Hydrogen fuel cells: overview



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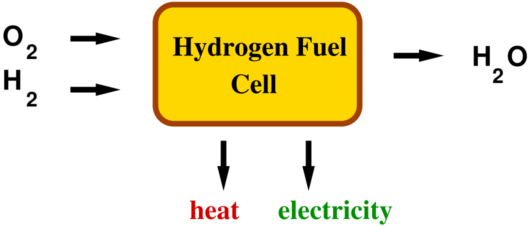

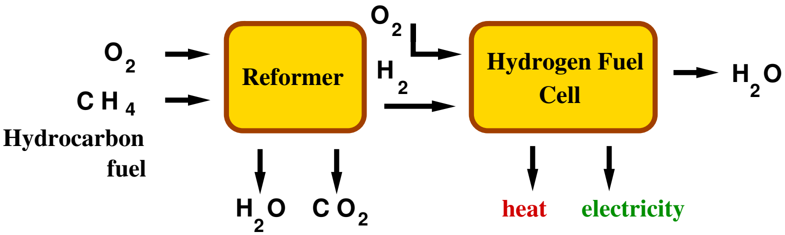

Palladium: the element

palladium[1] (pə-lā′dē-əm) **n.**
Symbol **Pd**
1. A soft, ductile, steel-white, tarnish-resistant, metallic element occurring naturally with platinum, especially in gold, nickel, and copper ores. Because it can absorb large amounts of hydrogen, it is used as a purification filter for hydrogen and a catalyst in hydrogenation. It is alloyed for use in electric contacts, jewelry, nonmagnetic watch parts, and surgical instruments. Atomic number 46; atomic weight 106.4; melting point 1,552° C; boiling point 3,140° C; specific gravity 12.02 (20° C); valence 2, 3, 4. See note at **element**.

[From **Pallas** (discovered at the same time as the element)]

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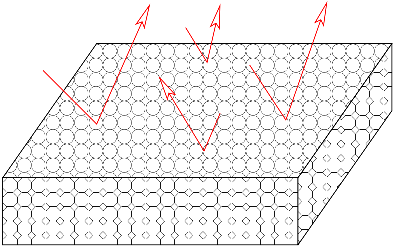
[From **Pallas** (discovered at the same time as the element)]

Pallas (p**ă**l′əs) **n.**
1. One of the largest asteroids, the second to be discovered.
2. *Greek Mythology* Athena.

[After **Pallas** (Athena)]

The Hydrogen-Palladium interface

Γ_0 = rate of hydrogen molecules impacting a surface
Representative value: 10^{19} hits/cm^2/sec
Γ_0 *proportional* to pressure



Around 10^{14} surface sites/cm^2

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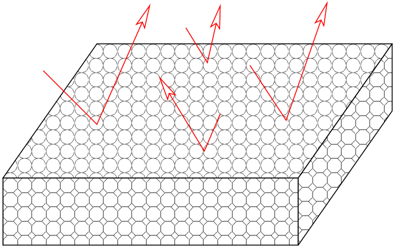

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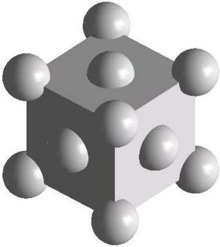


Modeling the surface layer

Fraction of occupied surface sites on the surface $= \alpha, \quad 0 \le \alpha \le 1$
Rate of sticking $= \Gamma_0 S_0 (1-\alpha)^2, \quad S_0 \approx 0.3$
Rate of recombination $= k_d \alpha^2$

Equilibrium:

$$\Gamma_0 S_0 (1-\alpha)^2 = k_d \alpha^2 \quad \Rightarrow \quad \left(\frac{1-\alpha}{\alpha}\right)^2 = \frac{k_d}{\Gamma_0 S_0}$$

Fraction of occupied interior sites $= \beta, \quad 0 \le \beta \le 1$
Flow rate from surface to interior $= k_i \alpha (1-\beta)$
Flow rate from interior to surface $= k_o \beta (1-\alpha)$

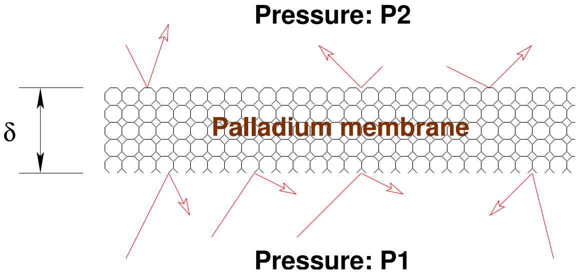
Equilibrium:

$$k_i \alpha (1-\beta) = k_o \beta (1-\alpha) \quad \Rightarrow \quad \frac{1-\alpha}{\alpha} = \frac{k_i}{k_o} \frac{1-\beta}{\beta}$$

Eliminate α: $$\frac{\beta}{1-\beta} = \frac{k_i}{k_o} \sqrt{\frac{\Gamma_0 S_0}{k_d}}$$

Diffusion through a membrane

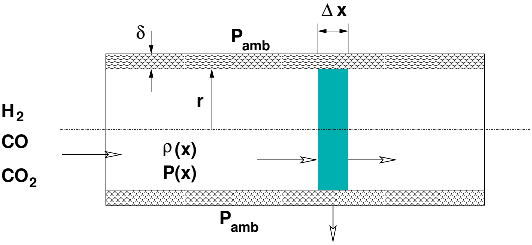
$$\beta \approx 0 \quad \Rightarrow \quad \beta = C_1\sqrt{\Gamma_0} = C_2\sqrt{P}$$



Concentrations near the surfaces: $C_2\sqrt{P_1}$ and $C_2\sqrt{P_2}$

$$\text{Flux} = \kappa\,\frac{\sqrt{P_1} - \sqrt{P_2}}{\delta}$$

Flow through a tube



$$\textbf{inflow} = \rho A v \qquad\qquad \textbf{outflow} = (\rho + \Delta\rho) A v$$

$$\textbf{leakage} = (2\pi r \Delta x)\kappa \frac{\sqrt{P} - \sqrt{P_{\mathrm{amb}}}}{\delta}$$

Conservation of mass

$$\rho A v = (\rho + \Delta\rho) A v + (2\pi r \Delta x)\kappa \frac{\sqrt{P} - \sqrt{P_{\mathrm{amb}}}}{\delta}$$

Differential equation of pressure

Conservation of mass

$$\frac{d\rho}{dx} = -\frac{2\pi r\kappa}{Av\delta}\left(\sqrt{P} - \sqrt{P_{\mathrm{amb}}}\,\right)$$

Ideal Gas

$$P = RT\rho$$

$$\frac{dP}{dx} = -\frac{2\pi r\kappa RT}{Av\delta}\left(\sqrt{P} - \sqrt{P_{\mathrm{amb}}}\,\right)$$

Differential equation

$$\boxed{\frac{dP}{dx} = -K\left(\sqrt{P} - \sqrt{P_{\mathrm{amb}}}\,\right),} \qquad K = \frac{2\pi r\kappa RT}{F\delta}, \quad F = Av$$

Calculation of pressure

$$\frac{dP}{dx} = -K\left(\sqrt{P} - \sqrt{P_{\mathrm{amb}}}\,\right)$$

Calculation of pressure

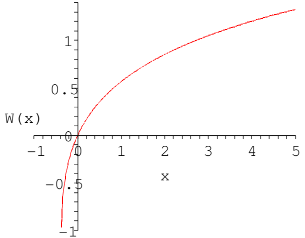
$$\frac{dP}{dx} = -K\left(\sqrt{P} - \sqrt{P_{\mathrm{amb}}}\,\right)$$

Solve for $P(x)$: $$P(x) = P_{\mathrm{amb}}[1 + W(z)]^2$$

$$\text{where } z = \frac{\sqrt{P(0)} - \sqrt{P_{\mathrm{amb}}}}{\sqrt{P_{\mathrm{amb}}}} \exp\left(\frac{\sqrt{P(0)} - \sqrt{P_{\mathrm{amb}}} - \frac{1}{2}Kx}{\sqrt{P_{\mathrm{amb}}}}\right)$$

W: the *Lambert function*

$ye^y = x \quad \Leftrightarrow \quad y = W(x)$



Efficiency of hydrogen exchange

Rate of hydrogen inflow $= F\rho(0)$

Rate hydrogen outflow $= F\rho(L)$

Rate of hydrogen release: $F\rho(0) - F\rho(L)$

Efficiency:

$$\mathcal{E} = \frac{\text{rate of hydrogen release}}{\text{rate of hydrogen inflow}} = \frac{F\rho(0) - F\rho(L)}{F\rho(0)} = 1 - \frac{\rho(L)}{\rho(0)} = 1 - \frac{P(L)}{P(0)}$$

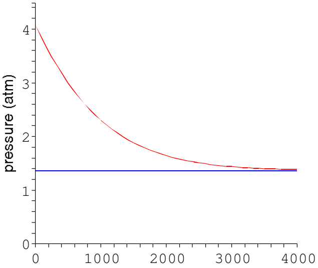
Best possible efficiency:

$$\mathcal{E}_{\mathsf{max}} = 1 - \frac{P_{\mathrm{amb}}}{P(0)}$$

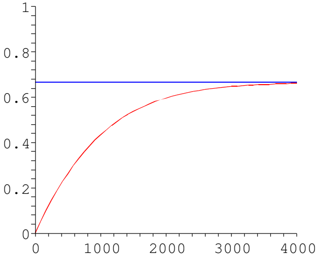
Numbers

tube radius	r	0.3175 cm
tube wall thickness	δ	0.0003 cm
flow rate	F	8330 cm^3/sec
inlet pressure	$P(0)$	4.08 atm
ambient pressure	P_{amb}	1.36 atm
temperature	T	673 Kelvin
diffusivity	κ	$6.96\ 10^{-8}$ mol/(cm sec $\text{atm}^{1/2}$)
gas constant	R	cm^3 atm / (mol Kelvin)

Results

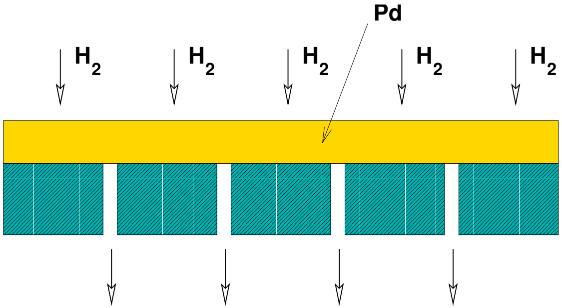


pressure (atm)
0
1
2
3
4
0
1000
2000
3000
4000



0
0.2
0.4
0.6
0.8
1
0
1000
2000
3000
4000

Membrane on porous support



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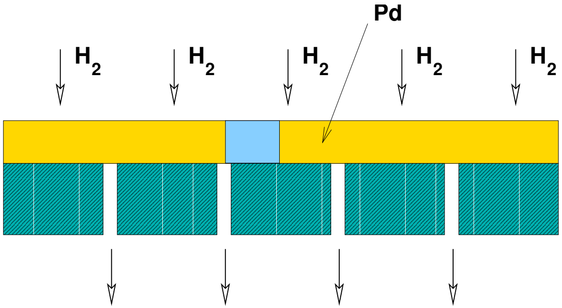

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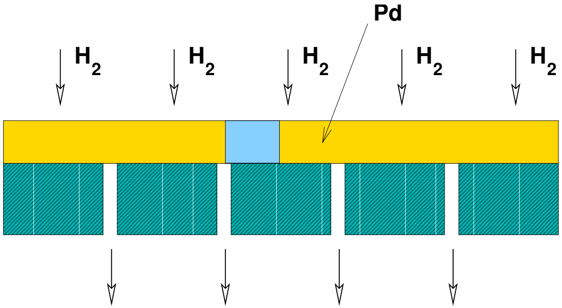
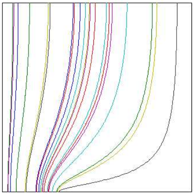
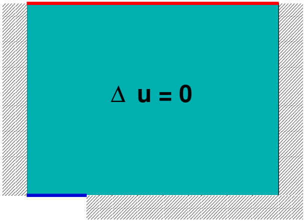
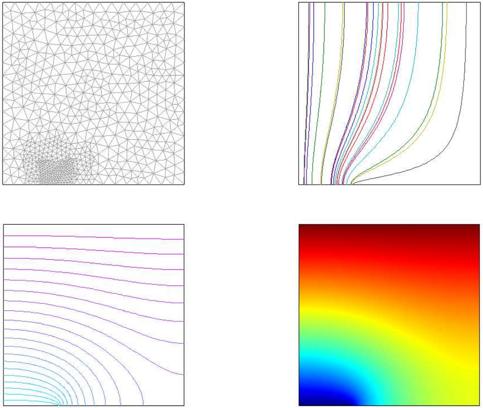






Numerical solution with Femlab



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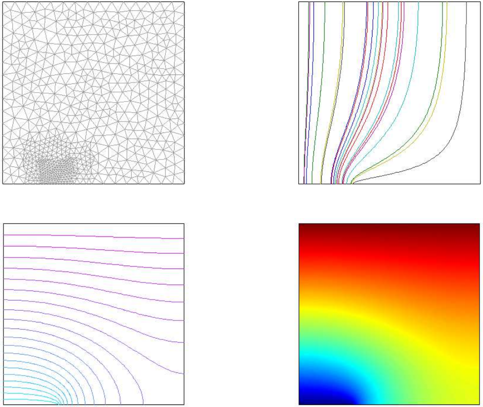
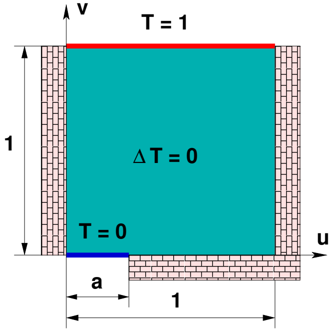


$$\int_0^1 \frac{\partial T}{\partial y}(x,1)\,dx = 0.667 \qquad \int_0^{0.3} \frac{\partial T}{\partial y}(x,0)\,dx = 0.627$$

The limiting case

$$\text{Throughput} = J(a) = \int_0^a \frac{\partial T}{\partial v}\bigg|_{v=0} du$$



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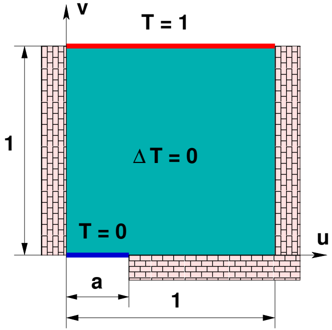
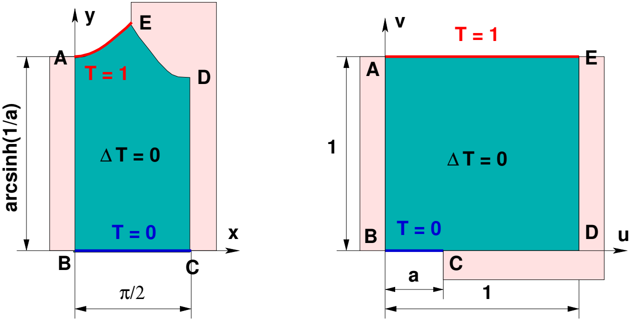


Theorem

Asymptotically, as $a \to 0$*:*

$$J(a) \approx \frac{\pi}{2 \ln \frac{2}{a}}.$$

Conformal mapping



$$u + iv = a\sin(x + iy) \quad \Leftrightarrow \quad u = a\sin x\cosh y, \quad v = a\cos x\sinh y$$

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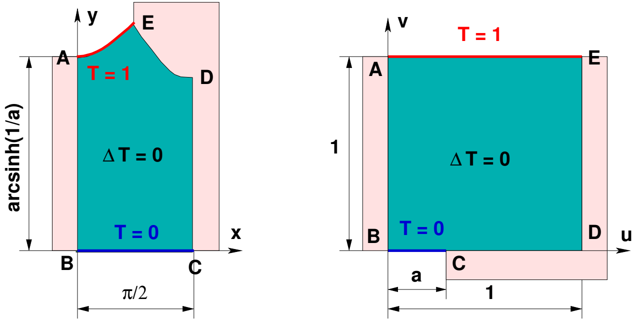

$$u + iv = a\sin(x + iy) \quad \Leftrightarrow \quad u = a\sin x\cosh y, \quad v = a\cos x\sinh y$$

$$T = T(x, y) \approx \frac{y}{\operatorname{arcsinh}(1/a)}$$

Proof of theorem

$$T(u, v) \approx \frac{1}{\operatorname{arcsinh}\frac{1}{a}} \operatorname{arccosh}\left[\frac{1}{2}\sqrt{\left(\frac{u}{a}+1\right)^2+\left(\frac{v}{a}\right)^2}+\frac{1}{2}\sqrt{\left(\frac{u}{a}-1\right)^2+\left(\frac{v}{a}\right)^2}\right]$$

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$$J(a) = \int_0^a \left.\frac{\partial T(u,v)}{\partial v}\right|_{v=0} du = ?$$

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$$\left.\frac{\partial T(u,v)}{\partial v}\right|_{v=0} = \frac{1}{a \operatorname{arcsinh}\frac{1}{a}} \frac{1}{\sqrt{1-(\frac{u}{a})^2}}$$

(calculus challenge!)

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$$J(a) = \int_0^a \left.\frac{\partial T(u,v)}{\partial v}\right|_{v=0} du = \frac{\pi}{2\operatorname{arcsinh}\frac{1}{a}} \approx \frac{\pi}{2\ln\frac{2}{a}} \qquad QED$$