# Pd in Au diffusion model

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## Problem Formulation

**Overall Goal:** Find (1) the amount of $Pd$ that diffuses to the first layer under given pressure, and (2) the kinetics of the diffusion of $Pd$ between the first and second layer, as well as the kinetics of adsorption of $CO$ on the $Pd$ in the first layer.

### Definitions

1. $Pd_i$ - Pd in layer $i$, for $i = 1, 2$
2. $Pd_1^{CO}$ - Pd in layer 1 with adsorbed $CO$
3. $\theta$ - Total coverage of $Pd$ in the $Au$ structure
4. $\theta_t^M$ - Coverage of species $M$ at time $t$
5. $\boldsymbol{\theta}_{1:T}^M$ - a vector containing the coverage of $M$ for all $t = 1, \ldots, T$
6. $P_t^{CO}$ - Pressure from $CO$ at time $t$
7. $\mathbf{p}_{1:T}$ - a vector containing $P_t^{CO}$, for all $t = 1, \ldots, T$
8. $k_{MN}$ - Rate constant from species $M$ to $N$
9. $\mathbf{k}$ - a vector containing all the rate constants involved in a reaction
10. $r_t^M$ - Reaction rate of species $M$ at time $t$.
11. $\mathbf{r}_{1:T}^M$ - a vector containing $r_t^M$ for all $t = 1, \ldots, T$.

### Chemical Equation

$$\mathrm{Pd_2} \underset{\mathrm{k_{12}}}{\overset{\mathrm{k_{21}}}{\rightleftharpoons}} \mathrm{Pd_1} \underset{\mathrm{k_{CO_1}}}{\overset{\mathrm{k_{1CO}}}{\rightleftharpoons}} \mathrm{Pd_1}^{\mathrm{CO}} \tag{1}$$

$$\mathrm{A} \underset{\mathrm{k_{BA}}}{\overset{\mathrm{k_{AB}}}{\rightleftharpoons}} \mathrm{B} \underset{\mathrm{k_{CB}}}{\overset{\mathrm{k_{BC}}}{\rightleftharpoons}} \mathrm{C} \tag{2}$$

where we let $A = Pd_2$, $B = Pd_1$, and $C = Pd_1^{CO}$, and their respective rate constants $k_{AB} = k_{21}$, $k_{BA} = k_{12}$, $k_{BC} = k_{1CO}$, and $k_{CB} = k_{CO_1}$.

### Reaction Rate Equations

$$\begin{aligned}
r_t^A &= -k_{AB}\theta_t^A + k_{BA}\theta_t^B \\
r_t^B &= -(k_{AB} + k_{BC})\theta_t^B + k_{AB}\theta_t^A + k_{CB}\theta_t^C \\
r_t^C &= -k_{CB}\theta_t^C + k_{BC}\theta_t^B
\end{aligned} \tag{3}$$

### Goal

Unknowns: $\mathbf{\Theta} = \left\{\boldsymbol{\theta}_{1:T}^B, \mathbf{k}, \mathbf{r}_{1:T}^A, \mathbf{r}_{1:T}^B, \mathbf{r}_{1:T}^C\right\}$

Knowns: $\mathbf{Y} = \left\{\boldsymbol{\theta}_{1:T}^C, \theta, \mathbf{p}_{1:T}\right\}$

Ranges:
$0 \le \theta_t^B \le 1,$

$0 \le \theta_t^C \le \theta_t^B, \quad$ for $t = 1, \ldots, T$.

Relations:
$\theta_t^A + \theta_t^B + \theta_t^C = \theta$

$\delta_t = \theta_t^A + \theta_t^B = \theta - \theta_t^C.$

## Proposed Model I (Coverage)

Model $\mathcal{M}_1$:

$$\begin{aligned}
\theta_t^B &= \theta_{t-1}^B e^{-\frac{\alpha}{P_t^{CO}}} + noise_{1t} \\
\theta_t^C &= \beta_t \theta_t^B + noise_{2t}
\end{aligned} \tag{4}$$

Let $\gamma_t = e^{-\frac{1}{P_t^{CO}}}$, so we can rewrite the model as

$$\begin{aligned}
\theta_t^B &= \theta_{t-1}^B \gamma_t^\alpha + noise_{1t} \\
\theta_t^C &= \beta_t \theta_t^B + noise_{2t}
\end{aligned} \tag{5}$$

where $0 \le \beta_t \le 1$, for $t = 1, \ldots, T$.

Unknowns: $\mathbf{\Theta}_{\mathcal{M}_1} = \left\{\boldsymbol{\theta}_{1:T}^B, \alpha, \boldsymbol{\beta}_{1:T}\right\}$

Given: $\mathbf{Y}_{\mathcal{M}_1} = \left\{\boldsymbol{\theta}_{1:T}^C, \theta, \mathbf{p}_{1:T}\right\}$

## Proposed Model II (Reaction rate)

Unknowns: $\mathbf{\Theta}_{\mathcal{M}_2} = \left\{\mathbf{k}, \mathbf{r}_{1:T}^B, \mathbf{r}_{1:T}^C\right\}$

Given: $\mathbf{Y}_{\mathcal{M}_2} = \left\{\boldsymbol{\theta}_{1:T}^C, \boldsymbol{\theta}_{1:T}^B, \boldsymbol{\theta}_{1:T}^A, \theta, \boldsymbol{\gamma}_{1:T}^\alpha\right\}$

Model $\mathcal{M}_2$:

$$\begin{aligned}\begin{bmatrix} r_t^B \\ r_t^C \end{bmatrix} &= \begin{bmatrix} \gamma_t^\alpha & 0 \\ 0 & \gamma_t^\alpha \end{bmatrix} \begin{bmatrix} r_{t-1}^B \\ r_{t-1}^C \end{bmatrix} + \begin{bmatrix} C_t^B \\ C_t^C \end{bmatrix} + noise_{3t} \\ \begin{bmatrix} \theta_t^B \\ \theta_t^B \end{bmatrix} &= \begin{bmatrix} \frac{1}{k_{AB}+k_{BC}} & 0 \\ 0 & \frac{1}{k_{BC}} \end{bmatrix} \begin{bmatrix} r_t^B \\ r_t^C \end{bmatrix} + \begin{bmatrix} D_t^B \\ D_t^C \end{bmatrix} + noise_{4t}\end{aligned} \tag{6}$$

where we get the system of 4 equations with 4 unknowns

$$C_t^B = -k_{AB}(\gamma_t^\alpha \delta_{t-1} - \delta_t) - k_{CB}(\gamma_t^\alpha \theta_{t-1}^C - \theta_t^C) \qquad D_t^B = \frac{k_{AB}}{k_{BA}+k_{BC}}\theta_t^A + \frac{k_{CB}}{k_{BA}+k_{BC}}$$

$$C_t^C = k_{CB}(\gamma_t^\alpha \delta_{t-1} - \delta_t) \qquad D_t^C = \frac{k_{CB}}{k_{BC}}\theta_t^C$$

A more compact form of the model can be written as

$$\begin{aligned}\mathbf{r}_t &= \mathbf{\Gamma}_t \mathbf{r}_{t-1} + noise_{3t} \\ \boldsymbol{\theta}_t^B &= \mathbf{H}\mathbf{r}_t + noise_{4t}\end{aligned} \tag{7}$$

with $\mathbf{r} = \begin{bmatrix} r_{t-1}^B \\ r_{t-1}^C \end{bmatrix}$, $\boldsymbol{\theta}_t^B = \begin{bmatrix} \theta_t^B \\ \theta_t^B \end{bmatrix}$, $\mathbf{\Gamma}_t = \begin{bmatrix} \gamma_t^\alpha & 0 \\ 0 & \gamma_t^\alpha \end{bmatrix}$, and $\mathbf{H} = \begin{bmatrix} \frac{1}{k_{AB}+k_{BC}} & 0 \\ 0 & \frac{1}{k_{BC}} \end{bmatrix}$.

## Challenges / Questions

1. What is all the prior information we know? (ranges of parameters, expected outcomes, existing relations/equations etc.)

2. Do we expect any $Pd$ to diffuse into layer 3 or further?

3. How to model the noise?

4. Is this enough data to find all unknowns?

5. Simultaneously estimating static and dynamic parameters.

6. Can we be sure that the pressure was off long enough for all of the $CO$ to desorb from the $Pd$?

7. If so, can we be sure that the pressure was off long enough for all of the $Pd$ has moved back to layer 2?

8. Is there a better observation equation we can use in model $\mathcal{M}_2$?

## Skip

Model $\mathcal{M}_2$:

$$
\begin{aligned}
\begin{bmatrix} r_t^A \\ r_t^B \\ r_t^C \end{bmatrix} &= \begin{bmatrix} \gamma_t^\alpha & 0 & 0 \\ 0 & \gamma_t^\alpha & 0 \\ 0 & 0 & \gamma_t^\alpha \end{bmatrix} \begin{bmatrix} r_{t-1}^A \\ r_{t-1}^B \\ r_{t-1}^C \end{bmatrix} + \begin{bmatrix} C_t^A \\ C_t^B \\ C_t^C \end{bmatrix} + noise_{3t} \\
\begin{bmatrix} \theta_t^B \\ \theta_t^B \\ \theta_t^B \end{bmatrix} &= \begin{bmatrix} \frac{1}{k_{BA}} & 0 & 0 \\ 0 & \frac{1}{k_{AB}+k_{BC}} & 0 \\ 0 & 0 & \frac{1}{k_{BC}} \end{bmatrix} \begin{bmatrix} r_t^A \\ r_t^B \\ r_t^C \end{bmatrix} + \begin{bmatrix} D_t^A \\ D_t^B \\ D_t^C \end{bmatrix} + noise_{4t}
\end{aligned} \tag{8}
$$

where

$$
\begin{aligned}
C_t^A &= k_{AB}(\gamma_t^\alpha \delta_{t-1} - \delta_t) \\
C_t^B &= -k_{AB}(\gamma_t^\alpha \delta_{t-1} - \delta_t) - k_{CB}(\gamma_t^\alpha \theta_{t-1}^C - \theta_t^C) \\
C_t^C &= k_{CB}(\gamma_t^\alpha \delta_{t-1} - \delta_t)
\end{aligned} \tag{9}
$$

and

$$
\begin{aligned}
D_t^A &= \frac{k_{AB}}{k_{BA}} \theta_t^A \\
D_t^B &= \frac{k_{AB}}{k_{BA}+k_{BC}} \theta_t^A + \frac{k_{CB}}{k_{BA}+k_{BC}} \\
D_t^C &= \frac{k_{CB}}{k_{BC}} \theta_t^C
\end{aligned} \tag{10}
$$