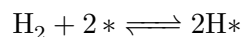


Carefully and neatly document your answers. You may use a mathematical solver like Jupyter/iPython. Use plotting software for all plots.

## 1 No need to look below the surface

One method of determining the surface area of Pt catalysts is by surface titration with  $\text{H}_2$ .  $\text{H}_2$  is thought to adsorb dissociatively, one H atom per surface Pt:



1.1 Derive the Langmuir isotherm for dissociative adsorption of  $\text{H}_2$ .

1.2 The data below were obtained for isothermal  $\text{H}_2$  chemisorption on a 3% (w/w) Pt catalyst supported on  $\gamma$ -alumina (nominally  $\text{Al}_2\text{O}_3$ ). Does the data conform to a dissociative Langmuir adsorption model?

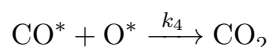
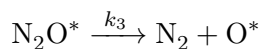
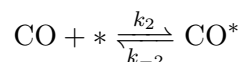
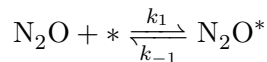
Pressure (bar)	mass $\text{H}_2$ /catalyst ( $\mu\text{g g}^{-1}$ )
0.0759	1.30
0.152	1.82
0.228	2.30
0.304	2.44
0.378	2.55
1.518	4.51
1.896	4.59
2.276	4.95
2.662	5.21
3.035	5.35
3.408	5.50
3.781	5.65

## 2 Langmuir, Hinshelwood, and company

Bob Davis and students (<https://doi.org/10.1006/jcat.1999.2780>) studied the reduction of nitrous oxide by carbon monoxide over a ceria-supported Rh catalyst. Following are rate data obtained at 543 K.

$P_{\text{CO}}$ (torr)	$P_{\text{N}_2\text{O}}$ (torr)	TOF ( $\text{s}^{-1}$ )
30.4	7.6	0.005
30.4	15.2	0.0091
30.4	30.4	0.018
30.4	45.6	0.023
30.4	76	0.036
7.6	30.4	0.039
15.2	30.4	0.024
45.6	30.4	0.012
76	30.4	0.0078

- 2.1 What is the apparent rate order with respect to CO? With respect to N<sub>2</sub>O?
- 2.2 Following is a candidate mechanism. Derive a Langmuir-Hinshelwood rate expression assuming the first two reactions are quasi-equilibrated and the third reaction is rate-limiting.



- 2.3 Use the observed data and regression to estimate the rate parameters. (*Hint:* Linearize to estimate the rate parameters, and use these as guesses for non-linear regression.)
- 2.4 The reaction rate is observed to be Arrhenius over the temperature range 500 to 550 K with apparent activation energy 140 kJ mol<sup>-1</sup>. Can you rationalize this result with your model?

### 3 Peak of the volcano

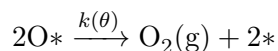
Ammonia synthesis ( $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ ) is among the most important heterogeneous catalytic reactions and has been studied extensively. Mehta (<https://doi.org/10.1021/acscatal.0c00684>) following Grabow write a simple lumped model for the mechanism over a metal catalyst:

	$E_a$ (eV)	$\Delta S^{\ddagger} = \Delta S^\circ$
$\text{N}_2 + 2* \rightleftharpoons 2\text{N}^*$	$1.57E_N + 1.56$	
$\text{N}^* + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3 + *$	$-0.39E_N + 1.24$	

The activation energies for both steps are related through a Brønsted-Evans-Polanyi relationship to the binding energy of N to the metal surface. Determine the rate per site (turnover frequency) at XX conditions from En X to Y. Typical catalysis Fe and Ru have binding energies X and Y.

### 4 Temperature programmed desorption

Temperature-programmed desorption (TPD) is a common way to explore the kinetics of desorption of gases from solid surfaces. Bray et al explored models for the associative desorption of O<sub>2</sub> from a Pt(111) surface, a process that has an activation barrier that depends on the coverage (<http://dx.doi.org/10.1016/j.susc.2013.12.005>):



Bray used a desorption prefactor of about  $1 \times 10^{14} \text{ s}^{-1}$  and found the desorption activation energy to depend approximately linearly on oxygen coverage, from 2.5 eV at zero coverage to 2.1 eV at 0.3 ML.

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- 4.1 Plot (on one graph) the  $\text{O}_2$  desorption rate vs temperature, starting from 0.0.073, 0.093, 0.164, 0.194, and 0.5 ML O and using a temperature ramp rate of  $8\text{ s}^{-1}$ .