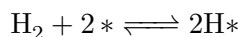Carefully and neatly document your answers. You may use a mathematical solver like Jupyter/iPython. Use plotting software for all plots.

1   Looking only at the surface

One method of determining the surface area of Pt catalysts is by surface titration with H_2. H_2 is thought to adsorb dissociatively, one H atom per surface Pt:

$$H_2 + 2* \rightleftharpoons 2H*$$

1.1   Derive the Langmuir isotherm for dissociative adsorption of H_2.

1.2   The data below were obtained for isothermal H_2 chemisorption on a 3% (w/w) Pt catalyst supported on γ-alumina (nominally Al_2O_3). Does the data conform to a dissociative Langmuir adsorption model?

Pressure (bar)	mass H_2/catalyst ($\mu g\,g^{-1}$)
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   Too hot to stick

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_2 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):

$$2O* \xrightarrow{k(\theta)} O_2(g) + 2*$$
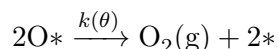
Bray used a desorption prefactor of about $1 \times 10^{14}\,s^{-1}$ and found the desorption activation energy to depend approximately linearly on oxygen coverage, from $2.5\,eV$ at zero coverage to $2.1\,eV$ at $0.3\,ML$.

2.1   Plot (on one graph) the 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 $8\,s^{-1}$.
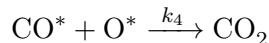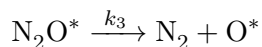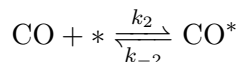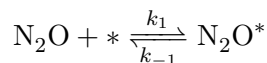
3   Langmuir, Hinshelwood, and company

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 $543\,\mathrm{K}$.

P_{CO} (torr)	P_{N_2O} (torr)	TOF (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

3.1 What is the apparent rate order with respect to CO? With respect to N_2O?

3.2 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.

$$N_2O + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O^*$$

$$CO + * \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO^*$$

$$N_2O^* \xrightarrow{k_3} N_2 + O^*$$

$$CO^* + O^* \xrightarrow{k_4} CO_2$$

3.3 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.)

3.4 The reaction rate is observed to be Arrhenius over the temperature range **500** to $550\,\mathrm{K}$ with apparent activation energy $140\,\mathrm{kJ\,mol^{-1}}$. Can you rationalize this result with your model?

4   Peak performance

Ammonia synthesis ($N_2 + 3H_2 \rightleftharpoons 2NH_3$) 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)	$\Delta S^{\circ\ddagger}$ (J/mol K)	ΔE (eV)	ΔS° (J/mol K)
$N_2 + 2* \rightleftharpoons 2N^*$	$1.57E_N + 1.56$	-216.9	$2E_N$	-216.9
$N^* + \frac{3}{2}H_2 \rightleftharpoons NH_3 + *$	$-0.39E_N + 1.24$	-5.6	$-0.55 - E_N$	-5.6

The activation energies for both steps are related through a Brønsted-Evans-Polanyi relationship to the binding energy of N, E_N. Those relationships are shown above, alone with some entropy data at 1 bar standard state. Note $k_B = 8.6173 \times 10^{-5}\,\mathrm{eV/K}$.

4.1 Determine and plot the log rate per site (turnover frequency) at $700\,\text{K}$, $100\,\text{bar}$, and a stoichiometric mixture of $\mathbf{N_2}$ and $\mathbf{H_2}$ at **1% conversion**, as a function of E_N from -1.3 to 0 **eV.** (***Hint***: First apply quasi-steady-state approximation to θ_N, then back solve for rate.)

4.2 Typical catalysis Fe and Ru have binding energies -1.2 and -0.5 **eV. Can you see why these are useful catalysts?**