

▼ Advanced Chemical Reaction Engineering (CBE 60546)

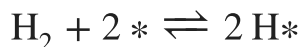
Homework 5

Due October 12, 2021

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

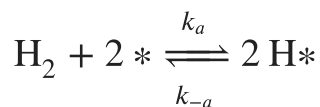
▼ 1 Looking only at the surface

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:



▼ 1.1 Derive the Langmuir isotherm for dissociative adsorption of H_2 .

Answer Here



The net rate of adsorption can then be expressed as:

$$r = k_a P_{H_2} C_*^2 - k_{-a} C_{H^*}^2$$

$$K_a = k_a/k_{-a}, \theta_* = 1 - \theta_{H^*}$$

At equilibrium, $r = 0$:

$$k_a P_{H_2} C_*^2 = k_{-a} C_{H^*}^2$$

$$K_a P_{H_2} = \theta_{H^*}^2 / (1 - \theta_{H^*})^2$$

Langmuir isotherm for dissociative adsorption of H_2 : $\theta_{H^*} = (K_a P_{H_2})^{1/2} / (1 + (K_a P_{H_2})^{1/2})$,

$$K_a = k_a/k_{-a}$$

- 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 ($\mu\text{g g}^{-1}$)
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

Answer Here

```
# assume there is only 1 g catalyst, so it has 0.03 g Pt catalyst
# use non-linear curve fit
```

```
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit
from sklearn.metrics import r2_score
```

```
Pressure=np.array([0.0759,0.152,0.228,0.304,0.378,1.518,1.896,2.276,
                    2.662,3.035,3.408,3.781])
H2mass=np.array([1.3,1.82,2.30,2.44,2.55,4.51,4.59,4.95,5.21,5.35,
                  5.5,5.65])
```

```
Pt_atomic_weight = 195.084 # Pt atomic weight
H2_weight = 2 # H atomic weight
```

```
n_total = 0.03/Pt_atomic_weight # total number of mole of Pt
H2_coverage = H2mass/10**6/H2_weight/n_total # H2 coverage
```

```
# plot H2 coverage vs pressure
plt.scatter(Pressure,H2_coverage,label='Experiment Data')
plt.xlabel('Pressure (bar)',fontsize=25)
plt.ylabel('$\\theta$',fontsize=25)
```

```
# non-linear curve fit to get K value.
def func(P,K):
    return (P*K)**0.5/(1+(K*P)**0.5)
```

```

popt, pcov = curve_fit(func, Pressure, H2_coverage)
#print(popt)

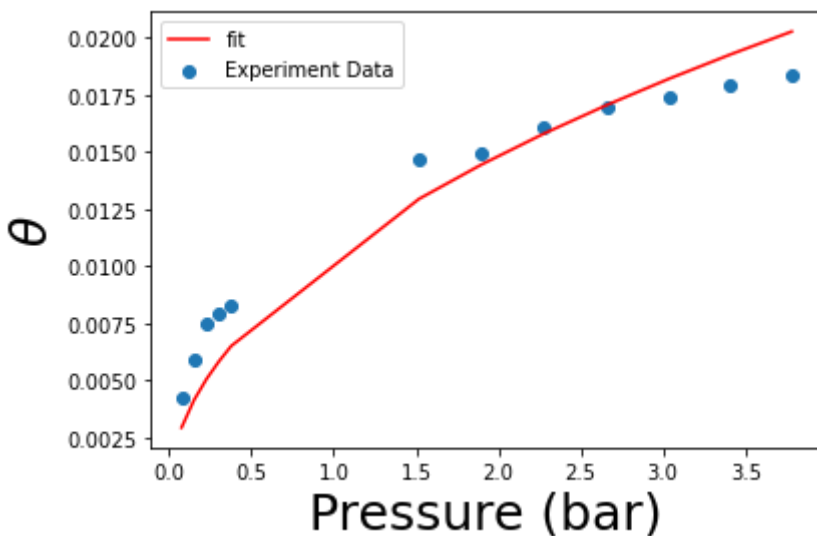
# then substitute K value back to function and use same pressure to get predict coverage
plt.plot(Pressure, func(Pressure, *popt), color='r', label = 'fit')
plt.legend()
print('R^2 : ', r2_score(H2_coverage, func(Pressure, *popt)))

```

R^2 : 0.9089871491080183

/var/folders/ws/sb9x3c5j7m5f4t70mq80mlrc0000gp/T/ipykernel_91429/3093961905

return (P*K)**0.5/(1+(K*P)**0.5)

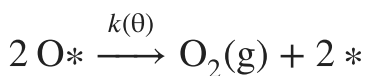


This plot shows clear systematic deviation from a Langmuir isotherm.

▼ 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 O₂ 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.

2.1 Plot (on one graph) the O₂ desorption rate vs temperature, starting from 0.0073, 0.093, 0.164, 0.194, and 0.5 ML O and using a temperature ramp rate of

8 Ks^{-1} .

Answer Here

Desorption rate expression is :

$$r_{\text{Des}} = -\frac{\partial \theta}{\partial T} = \nu * \theta^2 * \exp\left(\frac{-E(\theta)}{k_B T}\right)$$

ν is prefactor

θ has order 2 because this is secondary order desorption

$E(\theta)$ is activation energy

k_b is boltzmann constant

T is temperature related with time t and ramp rate β

$$T = T_0 + \beta t$$

In here, we use Euler method to integrate forward. [Euler Method](#)

```
# y= -(4/3)*x +2.5  Ea expression
```

```
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit
```

```
theta = [0.073,0.093,0.164,0.194,0.5] # unit (ML)
miu = 10**(14) # unit (/s)
beta = 8 # unit (K/s)
Kb = 8.6173*10**(-5)# unit(ev/k)
h = 0.1 # step size
t = np.arange(0,110,h) # time
rate = np.zeros(len(t))
Cov = np.zeros(len(t)) # coverage
```

```
for item in theta: # in this loop, first compute coverage vs T, the
```

```
    Theta=np.zeros(len(t))
    T=np.zeros(len(t))
    T[0]=400 # set initial T is 400K

    Theta[0]= item
    E=np.zeros(len(t)) # create np array for save activation energy
```

```
    for j in range(len(t)-1):
        T[j+1]=T[0]+ beta*t[j+1] # temperature change with time and ramp rate
        E[j]= (4/3)*Theta[j]-2.5
```

```
        Theta[j+1]=Theta[j]-h*(miu*Theta[j]**2)*np.exp(E[j]/(Kb*T[j])) # use Euler met
```

```
    Cov = np.c_[Cov,Theta] # add one coloum 'Theta' to Cov
```

```

Rdes=np.zeros(len(t))
for k in range (len(t)):
    Rdes[k]= (miu*Theta[k]**2)*np.exp(E[k]/(Kb*T[k])) # after get coverage vs T, v

rate =np.c_[rate,Rdes]

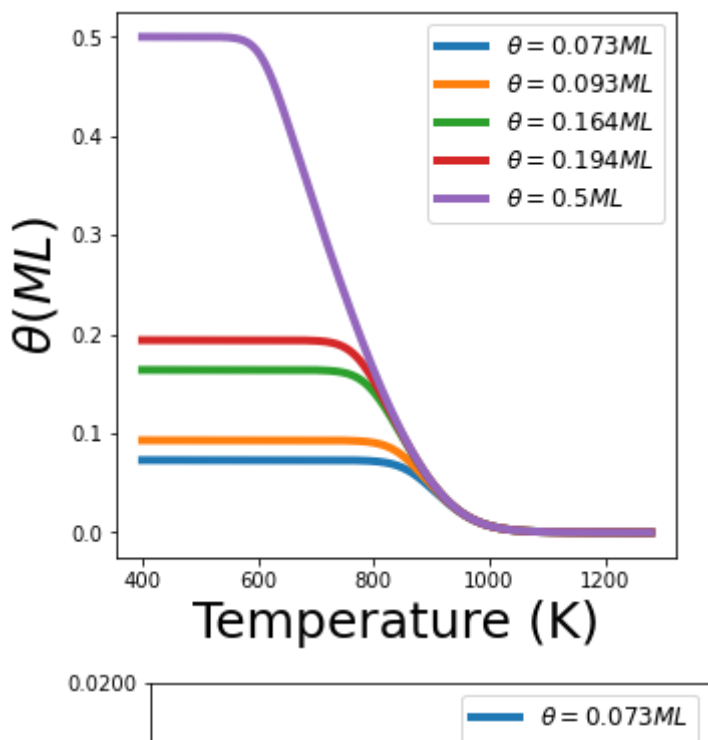
# plot Coverage vs T for different intial converage
plt.figure(figsize=(5,5))
plt.plot(T,Cov[:,1],label='$\\theta=0.073$ ML$',linewidth=4.0)
plt.plot(T,Cov[:,2],label='$\\theta=0.093$ ML$',linewidth=4.0)
plt.plot(T,Cov[:,3],label='$\\theta=0.164$ ML$',linewidth=4.0)
plt.plot(T,Cov[:,4],label='$\\theta=0.194$ ML$',linewidth=4.0)
plt.plot(T,Cov[:,5],label='$\\theta=0.5$ ML$',linewidth=4.0)

plt.ylabel('$\\theta$(ML)$',fontsize=25)
plt.xlabel('Temperature (K)',fontsize=25)
plt.legend(loc = 'upper right',prop={'size': 12})
plt.show()

# plot rate vs T for different intial converage
plt.figure(figsize=(5,5))
plt.plot(T,rate[:,1],label='$\\theta=0.073$ ML$',linewidth=4.0)
plt.plot(T,rate[:,2],label='$\\theta=0.093$ ML$',linewidth=4.0)
plt.plot(T,rate[:,3],label='$\\theta=0.164$ ML$',linewidth=4.0)
plt.plot(T,rate[:,4],label='$\\theta=0.194$ ML$',linewidth=4.0)
plt.plot(T,rate[:,5],label='$\\theta=0.5$ ML$',linewidth=4.0)

plt.ylabel('Rate(ML/s)',fontsize=25)
plt.xlabel('Temperature (K)',fontsize=25)
plt.ylim(0,0.02)
plt.xlim(350,1200)
plt.legend(loc = 'upper right',prop={'size': 12})
plt.show()

```



▼ 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 K.

P_{CO} (torr)	$P_{\text{N}_2\text{O}}$ (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 ?

Answer Here

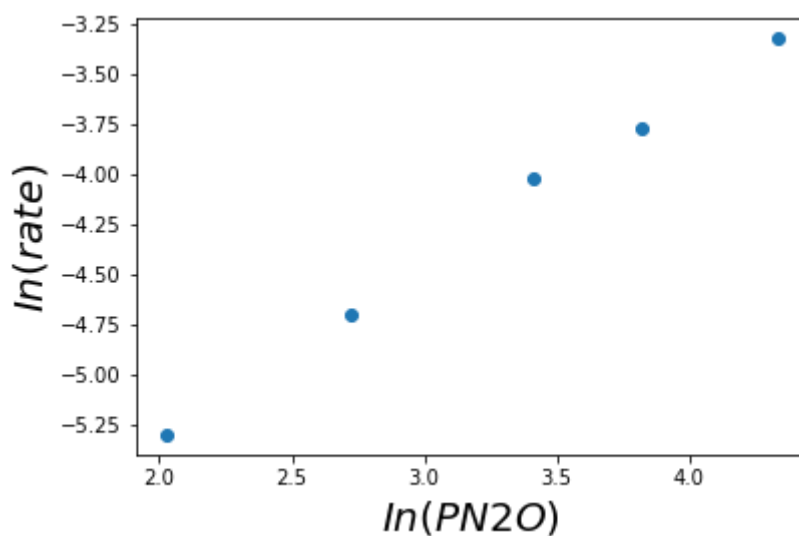
rate order =

$$\frac{\partial \ln(r)}{\partial \ln(PN_2O)} = \alpha$$

```
# Rate order of N2O, at constant pressure CO, plot ln(r) vs ln(PN2O)
PN2O=np.array([7.6,15.2,30.4,45.6,76])
TOF=np.array([0.005,0.0091,0.018,0.023,0.036])

plt.scatter(np.log(PN2O),np.log(TOF))
plt.xlabel(r'$\ln(PN_2O)$',fontsize=20)
plt.ylabel(r'$\ln(rate)$',fontsize=20)
plt.show()
print('Rate order of N2O is positive')

fit = np.polyfit(np.log(PN2O),np.log(TOF),1)
print('rate order of N2O is', fit[0])
```

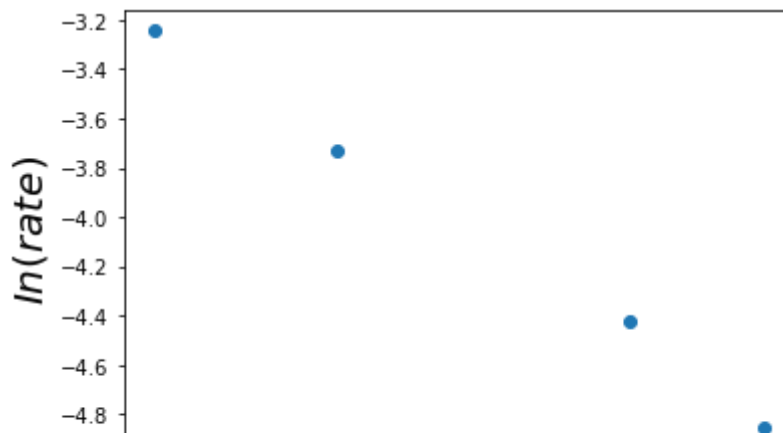


```
Rate order of N2O is positive
rate order of N2O is 0.8591286084841097
```

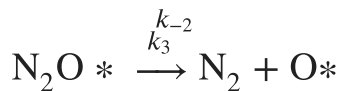
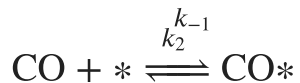
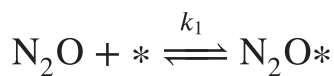
```
# Rate order of CO
PCO=np.array([7.6,15.2,45.6,76])
TOF=np.array([0.039,0.024,0.012,0.0078])

plt.scatter(np.log(PCO),np.log(TOF))
plt.xlabel(r'$\ln(PCO)$',fontsize=20)
plt.ylabel(r'$\ln(rate)$',fontsize=20)
plt.show()
print('Rate order of CO is negative')

fit = np.polyfit(np.log(PCO),np.log(TOF),1)
print('rate order of CO is', fit[0])
```



- 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.



Answer Here

from reaction 1:

$$\begin{aligned} r_1 &= k_1 * P_{\text{N}_2\text{O}} * \theta_* \\ r_{-1} &= k_{-1} * \theta_{\text{N}_2\text{O}} \end{aligned}$$

and reaction 1 is quasi equilibrium, so, $r_1 = r_{-1}$

from reaction 2:

$$\begin{aligned} r_2 &= k_2 * P_{\text{CO}} * \theta_* \\ r_{-2} &= k_{-2} * \theta_{\text{CO}} \end{aligned}$$

and reaction 2 is quasi equilibrium, so, $r_2 = r_{-2}$

based on those equilibrium equation and another site balance, you can solve

$$\theta_* = \frac{1}{K_{\text{N}_2\text{O}} * P_{\text{N}_2\text{O}} + K_{\text{CO}} * P_{\text{CO}} + 1}$$

from reaction 3:

$$r_3 = k_3 * \theta_{N_2O}$$

and from $r_1 = r_{-1}$, you can obtain relation between θ_{N_2O} with θ_*

and reaction 3 is rate-limiting step, you can express rate with reaction 3 using θ_*

$$rate = \frac{k_3 * K_{N_2O} * P_{N_2O}}{K_{N_2O} * P_{N_2O} + K_{CO} * P_{CO} + 1}$$

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.)

Answer Here

```

torr_to_bar = 0.00133322 # convert unit torr to bar
Pco = np.array([30.4,30.4,30.4,30.4,30.4,7.6,15.2,45.6,76])*torr_to_bar
Pn2o = np.array([7.6,15.2,30.4,45.6,76,30.4,30.4,30.4,30.4])*torr_to_bar
TOF=np.array([0.005,0.0091,0.018,0.023,0.036,0.039,0.024,0.012,0.0078])

```

To linearize, take reciprocal to rate expression in 3.2

Rr=1/TOF

```

def func(X, Kco, Kn2o, k3):
    x,y = X
    return (1/k3)+ (Kco/(k3*Kn2o))*x + (1/(k3*Kn2o))*y

```

```

ratio=Pco/Pn2o
rpn2o = 1/Pn2o

```

```

popt, pcov = curve_fit(func,(ratio,rpn2o),Rr,maxfev=6000)

```

```

print('KN2O =',popt[1])
print('KCO =',popt[0])
print('k3 =',popt[2])

```

```

KN2O = 130.39104467332157
KCO = 479.2638397342351
k3 = 0.0816047447101732

```

use above number as intial guess

```

def func(X, Kco, Kn2o, k3):
    x,y = X
    return (k3*Kn2o*x)/(Kn2o*x+Kco*y+1)

```

```
popt, pcov = curve_fit(func, (Pn2o, Pco), TOF, [popt[0], popt[1], popt[2]], maxfev=6000)

print('KN2O =', popt[1])
print('KCO =', popt[0])
print('k3 =', popt[2])

KN2O = 16.415666615916315
KCO = 131.69838869168254
k3 = 0.17222565397791414
```

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

Answer Here

From rate expression in section 3.2, the denominator has combination of P_{CO} and P_{N_2O} and 1, so it should not be perform arrhenius with temperature change. If reaction rate has arrhenius phenonema, then P_{CO} should be dominante in denominator, follows the rate order of P_{CO} is negative.

4 Peak performance

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)	ΔS^\ddagger (J/mol K)	ΔE (eV)	ΔS° (J/mol K)
$\text{N}_2 + 2 * \rightleftharpoons 2 \text{N} *$	$1.57E_N + 1.56$	-216.9	$2E_N$	-216.9
$\text{N} * + \frac{3}{2} \text{H}_2 \rightleftharpoons \text{NH}_3 + *$	$-0.39E_N + 1.24$	-5.6	$-0.55 - E_N$	-5.6

The activation energies for both steps are related through a Bronsted-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 $k_B = 8.6173 \times 10^{-5} \text{ eV/K}$.

4.1 Determine and plot the log rate per site (turnover frequency) at 700 K, 100 bar, and a stoichiometric mixture of N_2 and 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.)

Answer Here

```

P = 100                # bar
T = 700                # K
kb = 8.6173*10**(-5)   # unit(ev/k)
h = 6.582*10**(-16)    # unit(ev*s)

# 1 assume initial N2 = 1 mole, H2 = 3 mole
# 2 at 1% conversion, N2 = 0.99 mole, H2 = 2.97 mole, NH3 = 0.02 mole

tot=0.99+2.97+0.02

PN2 = P*(0.99/tot)
PH2 = P*(2.97/tot)
PNH3 = P*(0.02/tot)
print('-----')
print('N2 Pressure =',PN2,'bar')
print('H2 Pressure =',PH2,'bar')
print('NH3 Pressure =',PNH3,'bar')

-----
N2 Pressure = 24.87437185929648 bar
H2 Pressure = 74.62311557788945 bar
NH3 Pressure = 0.5025125628140703 bar

# now let's compute rate constant for reaction

EN = np.arange(-1.3,0,0.01)

# for reaction 1: N2+2*-->2N*

delS1_dag = -216.9/96490    #convert to ev/K, 1eV = 96.49kj/mole.

klf = np.zeros(len(EN))

for i in range(len(EN)):

    Ea1 = 1.57*EN[i] + 1.56

    if Ea1<=0:
        delG1_dag = 0-T*delS1_dag

```

```

k1f[i] = (kb*T/h)*np.exp(-1*delG1_dag/(kb*T))

if Ea1>0:
    delG1_dag = Ea1-T*delS1_dag
    k1f[i] = (kb*T/h)*np.exp(-1*delG1_dag/(kb*T))

delG10 = 2*EN - T*delS1_dag
K1 = np.exp(-1*delG10/(kb*T))

# k-1 = k1/K1
k1r = k1f/K1

# for reaction 2: N* + (3/2) H2 --> NH3 + *

delS2_dag = -5.6/96490 #convert to ev/K, 1eV = 96.49kj/mole.

k2f = np.zeros(len(EN))

for i in range(len(EN)):

    Ea2 = -0.39*EN[i] + 1.24

    if Ea2<0:
        delG2_dag = 0-T*delS2_dag
        k2f[i] = (kb*T/h)*np.exp(-1*delG2_dag/(kb*T))

    if Ea2>0:
        delG2_dag = Ea2-T*delS2_dag
        k2f[i] = (kb*T/h)*np.exp(-1*delG2_dag/(kb*T))

delG20 = (-0.55-EN) - T*delS2_dag

K2 = np.exp(-1*delG20/(kb*T))

# k-2 = k2/K2
k2r = k2f/K2

def thetaN(x):
    a = (2*k1f*PN2) - 2*k1r
    b = (-4*k1f*PN2)-(k2f*PH2**1.5)-(k2r*PNH3)
    c = (2*k1f*PN2) + k2r*PNH3
    return a*x**2+b*x+c

from scipy.optimize import fsolve

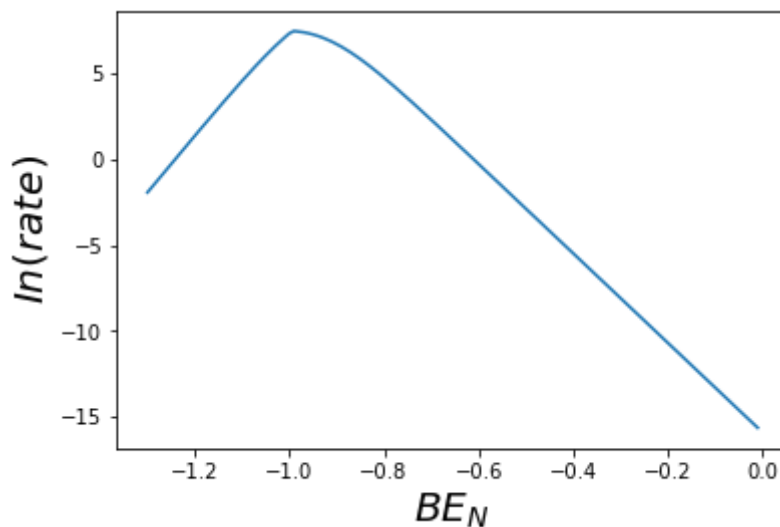
THETA = fsolve(thetaN, np.zeros(len(EN)))

rate = (k2f*THETA*PH2**1.5) - k2r*PNH3*(1-THETA)

```

```
plt.plot(EN,np.log(rate))
plt.xlabel(r'$BE_{N}$',fontsize=20)
plt.ylabel(r'$\ln(rate)$',fontsize=20)
```

```
Text(0, 0.5, '$\ln(rate)$')
```



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

Answer Here

Fe has -1.2 eV which is close to sabatier optimal area with higher rate.

Ru has -0.5 eV which is not close to optimal area because there are only 2 reaction steps, but paper has multiple reaction steps.