THERMODYNAMICS PROJECT REPORT

METALLURGICAL ENGINEERING AND MATERIALS SCIENCE DEPARTMENT
INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

By,

Swastika Agarwal(190110095)
Labdhi Gandhi (190110041)
Rutuja Thkaur (190110077)

Group number - G3_23
Problem no. - 9

Problem Statement

Write a program which gives stability of Fe_3O_4, FeO and Fe in a graph showing Temperature vs PH_2 / (pH_2+ PH_2O). Consider the range of temperature from 300K to 1500K.

ABSTRACT/INTRODUCTION

In this project, we have calculated the stability of Fe_3O_4, FeO and Fe between the temperature ranging from 300K to 1500K and have plotted the results accordingly using python

REACTIONS AND CALCULATIONS

$Fe + \frac{1}{2} * O_2 \rightarrow FeO$ ----------(1)

$\Delta G^0 = -259600 + 62.55*T$

$3*Fe + 2*O_2 \rightarrow Fe_3O_4$----------(2)

$\Delta G^0 = 1091000 - 312.8 * T$

$H_2 + \frac{1}{2}*O_2 \rightarrow H_2O$ ----------(3)

$\Delta G^0 = - 247300 + 55.9*T$

REACTION (4)

$FeO + H_2 \rightarrow Fe + H_2O$

$\Delta G^0 = 259600 - 62.55*T - 247300 + 55.9*T = 12300 - 6.65*T$

Considering equilibrium, $\Delta G = 0$

$12300 - 6.65 * T = -8.314 * T * \ln(PH_2O/PH_2)$

Let PH_2 be x, then $P(H_2O)$ will be 1 - x

On solving the equation we get, $x = \frac{1}{1 + exp(0.8 - \frac{1479.43}{T})}$

REACTION (5)

$Fe_3O_4 + 4*H_2 \rightarrow 3*Fe + 4*H_2O$

$\Delta G^0 = 1091000 - 312.8 * T + 4 * (- 247300 + 55.9 * T) = 101800 - 89.2 * T$

Considering equilibrium, $\Delta G = 0$

$101800 - 89.2 * T = -8.314 * T * \ln((PH_2O/PH_2)^4)$

Let PH_2 be x, then $P(H_2O)$ will be 1 - x

On solving the equation we get, $x = \frac{1}{1 + exp(2.68 - \frac{3061.1}{T})}$

REACTION (6)

$Fe_3O_4 + H_2 \rightarrow 3*FeO + H_2O$

$\Delta G^0 = 101800 - 89.2 * T - 3 * (123000 - 6.65 * T) = 64900 - 69.25 * T$

Considering equilibrium, $\Delta G = 0$

$64900 - 69.25 * T = -8.314 * T * \ln(PH_2O / PH_2)$

Let PH_2 be x, then $P(H_2O)$ will be 1 - x

On solving the equation we get, $x = \frac{1}{1 + exp(8.33 - \frac{7806.11}{T})}$

CONCLUSIONS

The 1st plot generated from the program shows Fe-O-H stability diagram
At the triple point (where all the three lines meet),
Fe_3O_4, FeO and Fe are in equilibrium. i.e.,
$Fe_3O_4 + Fe \rightarrow 4FeO$ ($\Delta G = 0$)
$\Delta G^0 = \Delta G^0$(reaction 3) - ΔG^0(reaction 1)
$\Delta G^0 = 101800 - 89.2 * T - 3 * (123000 - 6.65 * T) - 12300 + 6.65 * T = 52600 - 62.6 * T$
$\Delta G = \Delta G^0 - R * T * \ln(K)$
Equating ΔG to 0, we get $T = 52600 / 62.6 = 840.25$ K

This is a unique point with a temperature approximately 840K and $pH_2/(pH_2+pH_2O)$ approximately equal to 0.72.
Now at Temperature less than this invariant temperature we find
$Fe_3O_4 + Fe \rightarrow 4FeO$ ($\Delta G > 0$) or
$4FeO \rightarrow Fe_3O_4 + Fe$ ($\Delta G < 0$)
That means below 880K, irrespective of pH_2 / pH_2O value, FeO will always split to Fe_3O_4 and Fe.
Therefore, lines containing FeO will not be there below this temperature that is to the left of triple point. Blue and Green lines go away.
Above 880K,
$Fe_3O_4 + Fe \rightarrow 4FeO$ ($\Delta G < 0$)
if Fe_3O_4 and Fe come together, then they will spontaneously convert to FeO. Therefore, the Fe_3O_4, Fe line (Red Line) cannot be there.
Thus the diagram becomes as shown in 2nd plot generated from the program

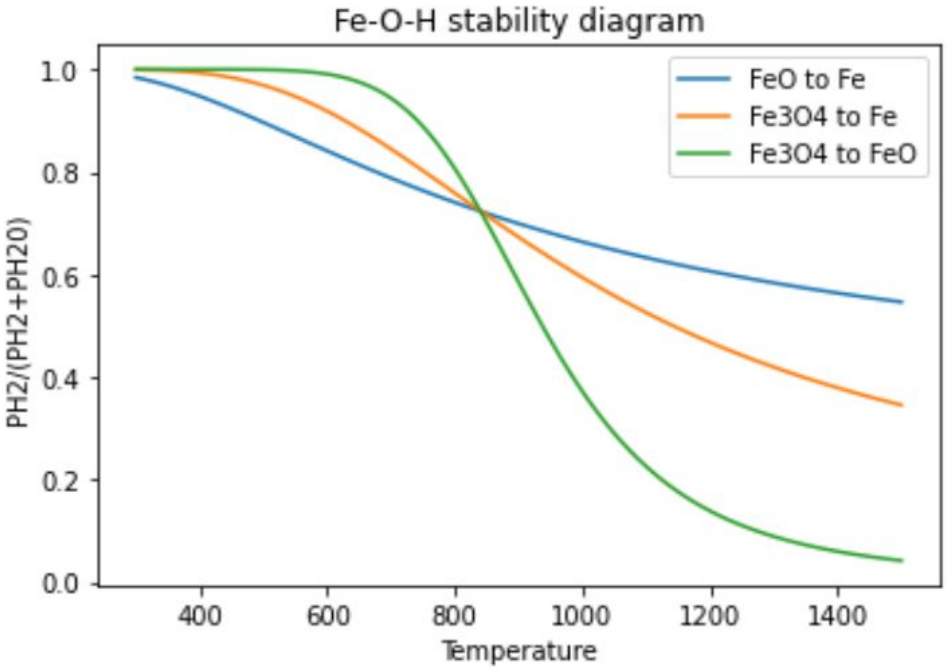
CODE

```python
import numpy as np
import matplotlib
import matplotlib.pyplot as plt

T = np.linspace(300,1500,100)

deltag0_1 = -259600 + 62.55*T  # for reaction of Fe and O2 to give FeO
deltag0_2 = -1091000 + 312.8*T  # for reaction of Fe and O2 to give Fe3O4
deltag0_3 = -247300 + 55.9*T  # for reaction of H2 and O2 to give H2O

# for reaction of FeO and H2 to give Fe and H2O
# deltag0_a = deltag0_1 + deltag0_3
deltag0_a = 12300 - 6.65*T
# x1 = 1/(1+(exp(-deltag0_a/(R*T))))
x1 = 1/(1+np.exp(0.8 - (1479.43/T)))
plt.plot(T,x1)

# for reaction of Fe3O4 and H2 to give Fe and H2O
# deltag0_b = deltag0_2 + 4*deltag0_3
deltag0_b = 101800 - 89.2*T
# x2 = 1/(1+((exp(-deltag0_b/(R*T)))/4))
x2 = 1/(1+np.exp(2.68 - (3061.1/T)))
plt.plot(T,x2)

# for reaction of Fe3O4 and H2 to give FeO and H2O
# deltag0_c = deltag0_b - 3*deltag0_a
deltag0_c = 64900 - 69.25*T
# x3 = 1/(1+(exp(-deltag0_c/(R*T))))
x3 = 1/(1+np.exp(8.33 - (7806.11/T)))
plt.plot(T,x3)

plt.xlabel("Temperature")
plt.ylabel("PH2/(PH2+PH20)")
plt.legend(('FeO to Fe','Fe3O4 to Fe','Fe3O4 to FeO'))
plt.title(" Fe-O-H stability diagram ")
plt.show()

T_invariant = (64900 - 12300)/(69.25 - 6.65) # from deltag0_c - deltag0_a = 0 that is ΔG = 0 for reaction Fe3O4 + Fe = 4FeO
print('Invarient temperature is',T_invariant)


T2 = np.linspace(T_invariant,1500,100)
plt.plot(T2, 1/(1+np.exp(0.8-(1479.43/T2))))

T1 = np.linspace(300,T_invariant,100)
plt.plot(T1, 1/(1+np.exp(2.68-(3061.1/T1))))

T2 = np.linspace(T_invariant,1500,100)
plt.plot(T2, 1/(1+np.exp(8.33-(7806.11/T2))))

plt.text(500, 0.5, 'Fe3O4', horizontalalignment='center', verticalalignment='center')
plt.text(1000, 0.9, 'Fe', horizontalalignment='center', verticalalignment='top')
plt.text(1200, 0.4, 'FeO', horizontalalignment='center', verticalalignment='bottom')
plt.xlabel("Temperature")
plt.ylabel("PH2/(PH2+PH20)")
plt.legend(('FeO to Fe','Fe3O4 to Fe','Fe3O4 to FeO'))
plt.title(" Fe-O-H stability diagram ")
plt.show()
```

Instructions to run the code :

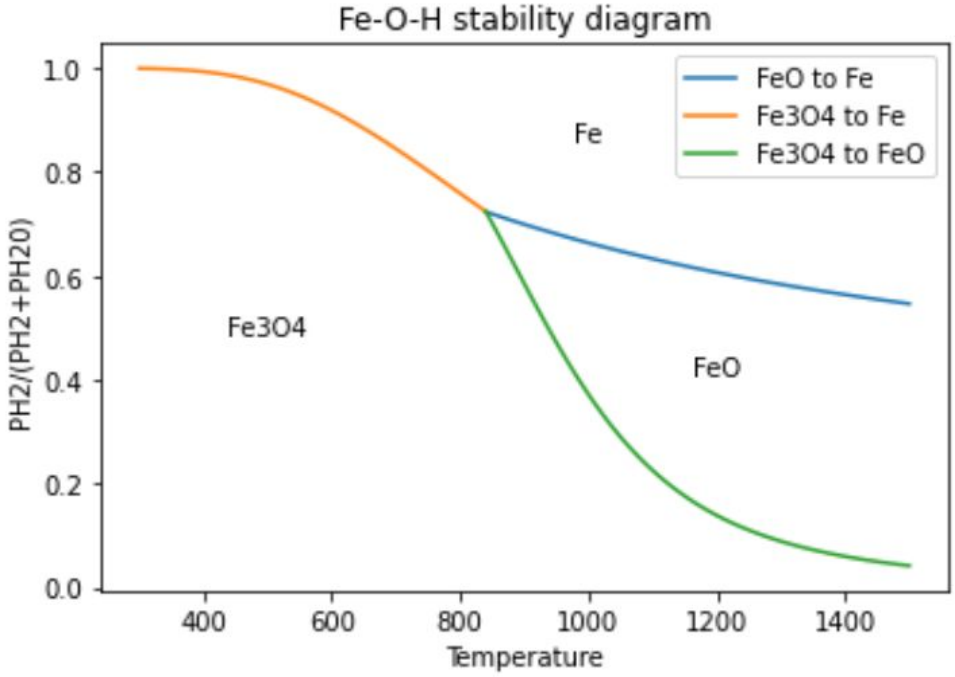
1. Go to this link for code(If it doesn't work then use this) and copy the code.
2. Open .py file in any python IDE with pre-installed MATPLOTLIB and NUMPY libraries.
3. Then paste the code and run it to get the required plots(also available below).

PLOT 1



PLOT 2

```
Invarient temperature is 840.2555910543131
```



CONTRIBUTION

ROLL NO.	CONTRIBUTION
JOINT CONTRIBUTION	Calculation of Critical temperature Report Making Adding comments in code
190110095 Swastika Agarwal	Calculation of reaction 4 Wrote code for the second plot first taking reaction REACTION 5 to be stable under 840 K and then REACTION 4 and REACTION 6 to be stable above 840 K that is considering below 840 K lines containing FeO will not be there and above 840 K Fe3O4, Fe line cannot be there as discussed in the above report.
190110041 Labdhi Gandhi	Calculation of reaction 5 Wrote code for showing the first plot assuming all the three reactions over the entire temperature range and labelled stability regions for Fe3O4,Fe and FeO for the second plot by taking into account that below 840 K lines containing FeO will not be there and above 840 K Fe3O4, Fe line cannot be there.
190110077 Rutuja Thakur	Calculation of reaction 6 Rechecked both the codes by Swastika and Labdhi and wrote the final code.

SOURCE OF DATA

Data related to free energy change for the REACTIONS 1,2 and 3 from website webbook.nist.gov and also took help from Question 9 of assignment 3.