Thermodynamics of Materials AD19:
Class Activity 03

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R. Gaskell, D., & E. Laughlin, D. (2018). Introcuction to the Thermodynamics of Materials. (C. Press, Ed.). Taylor & Francis Group.

Binary Phase Diagrams

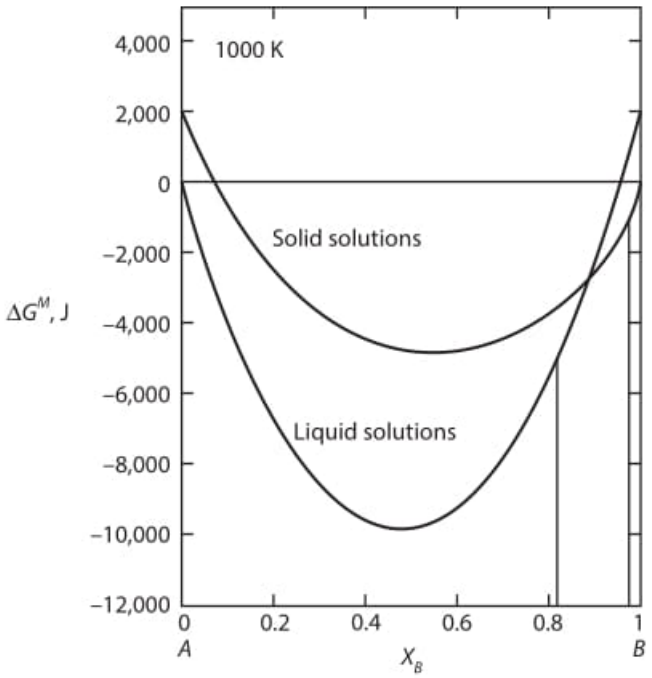
In [1]:

```
# PYTHON LIBRARIES
%matplotlib inline

import numpy as np
np.seterr(divide='ignore', invalid='ignore')
import pandas as pd
import matplotlib.pyplot as plt
plt.rc('xtick', labelsize=15)
plt.rc('ytick', labelsize=15)

from IPython.display import display, Image
from scipy.optimize import least_squares, fsolve, curve_fit
```

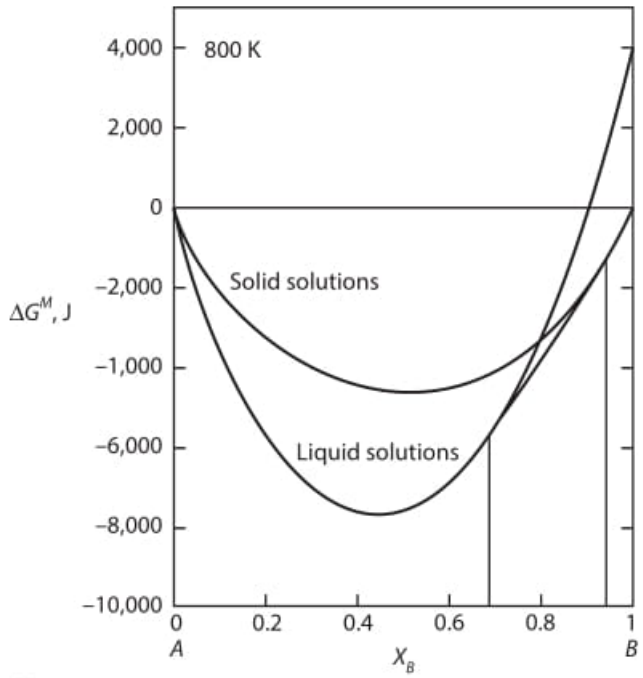
Let's reproduce Gaskell's plots:

In [2]:

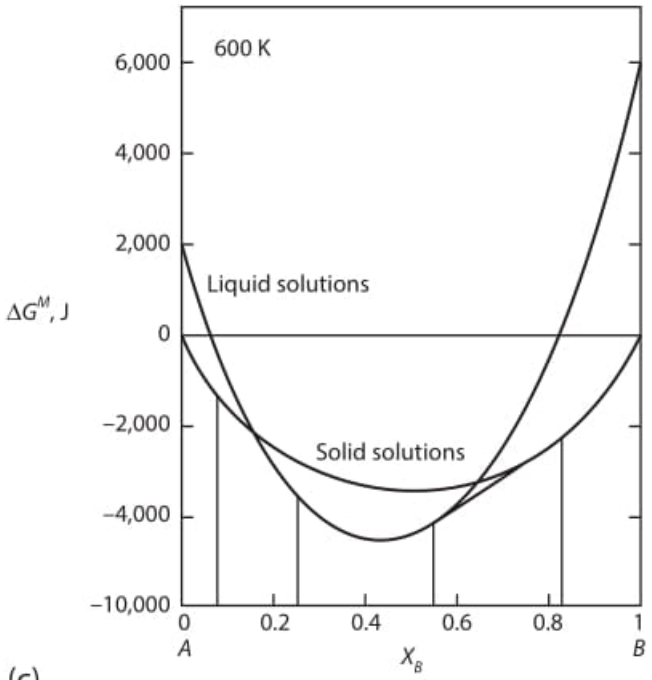
```
display(Image(filename='./img/ITTTOM-378.jpg'))
```


1000 K
4,000
2,000
0
−2,000
−4,000
−6,000
−8,000
−10,000
−12,000
ΔG^M, J
Solid solutions
Liquid solutions
0
0.2
0.4
0.6
0.8
1
A
X_B
B

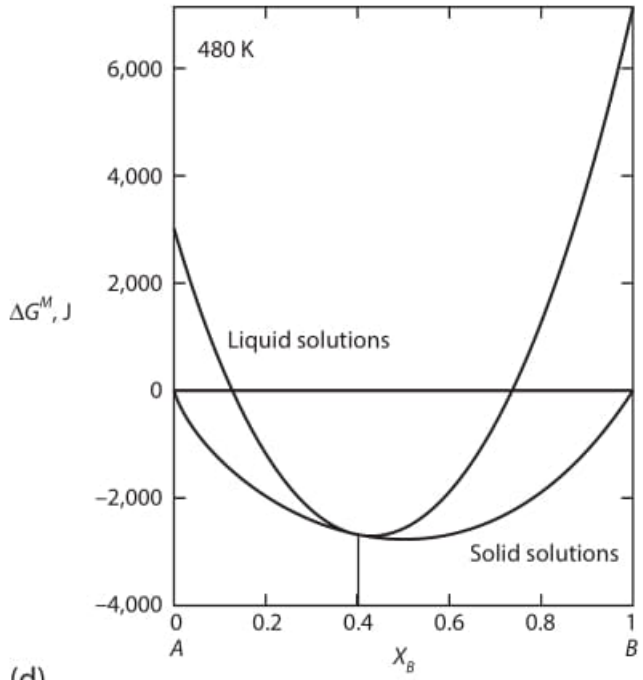
(a)


800 K
4,000
2,000
0
−2,000
−1,000
−6,000
−8,000
−10,000
ΔG^M, J
Solid solutions
Liquid solutions
0
0.2
0.4
0.6
0.8
1
A
X_B
B

(b)


600 K
6,000
4,000
2,000
0
−2,000
−4,000
−10,000
ΔG^M, J
Liquid solutions
Solid solutions
0
0.2
0.4
0.6
0.8
1
A
X_B
B

(c)


480 K
6,000
4,000
2,000
0
−2,000
−4,000
ΔG^M, J
Liquid solutions
Solid solutions
0
0.2
0.4
0.6
0.8
1
A
X_B
B

(d)

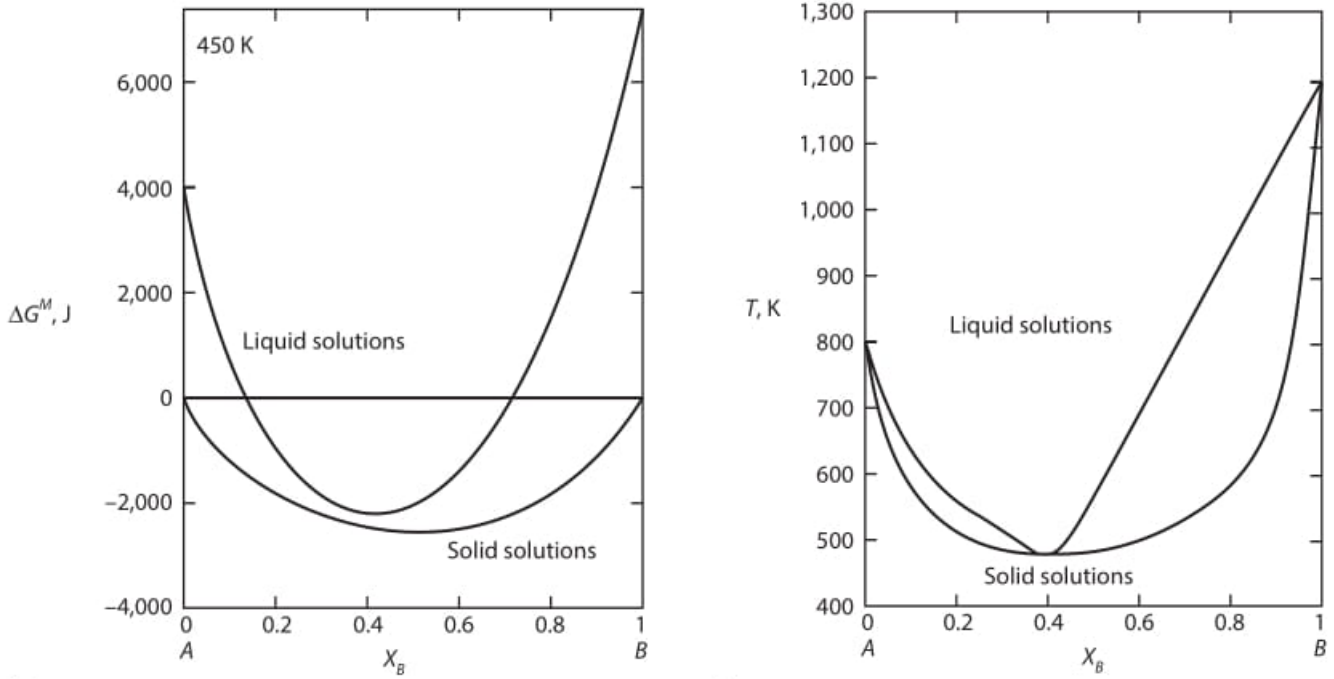


Figure 10.24 The molar Gibbs free energy of mixing curves at various temperatures, and the phase diagram for a binary system which forms regular solid solutions in which $\alpha_s = 0$ and regular liquid solutions in which $\alpha_l = -20{,}000$ J.

$$ \Delta G_{m,A} = 8000 - 10 T [J/mol] $$$$ \Delta G_{m,B} = 12000 - 10 T [J/mol] $$$$ \Omega_l = -20000 [J/mol] $$$$ \Omega_s = 0 [J/mol] $$$$ \Delta G_s = - x_A \Delta G_{m,A} + R T (x_A ln x_A + x_B ln x_B) + \Omega_s x_A x_B $$$$ \Delta G_l = x_B \Delta G_{m,B} + R T (x_A ln x_A + x_B ln x_B) + \Omega_l x_A x_B $$$$ G_{B,s} = 0 $$$$ G_{A,l} = 0 $$

Substituing numerical values ...

if T greater than $T_{m,(A)}$ and lower than $T_{m,(B)}$ then, the liquid is chosen as the standard state for A, and the solid is chosen as the standard state for B

$$ \Delta G_l = x_B (12000 - 10 T) + R T (x_A ln x_A + x_B ln x_B) - 20000 x_A x_B $$$$ \frac{d \Delta G_l}{d x_B} = R T (ln x_B - ln x_A)-10 T-20000 x_A + 20000 x_B + 12000 $$$$ \Delta G_s = - x_A (8000 - 10 T) + R T (x_A ln x_A + x_B ln x_B) $$$$ \frac{d \Delta G_s}{d x_B} = R T (ln x_B - ln x_A) - 10 T + 8000 $$

else if T lower than $T_{m,(A)}$ and lower than $T_{m,(B)}$ then, solid is chosen as the standard state

$$ \Delta G_l = x_A (8000 - 10 T) + x_B (12000 - 10 T) + R T (x_A ln x_A + x_B ln x_B) - 20000 x_A x_B $$$$ \frac{d \Delta G_l}{d x_B} = R T (ln x_B - ln x_A) - 20000 x_A + 20000 x_B + 4000 $$$$ \Delta G_s = R T (x_A ln x_A + x_B ln x_B) $$$$ \frac{d \Delta G_s}{d x_B} = R T (ln x_B - ln x_A) $$

else (if T greater than $T_{m,(A)}$ and greater than $T_{m,(B)}$ then), liquid is chosen as the standard state

$$ \Delta G_l = R T (x_A ln x_A + x_B ln x_B) - 20000 x_A x_B $$$$ \frac{d \Delta G_l}{d x_B} = R T (ln x_B - ln x_A) - 20000 x_A + 20000 x_B $$$$ \Delta G_s = - x_A (8000 - 10 T) - x_B (12000 - 10 T) + R T (x_A ln x_A + x_B ln x_B) $$$$ \frac{d \Delta G_s}{d x_B} = R T (ln x_B - ln x_A) - 4000 $$

In [3]:

```
#-------------------------------------------------------------#
### GIBBS FREE ENERGIES OF MIXING for the LIQUID SOLUTIONS ###
#-------------------------------------------------------------#

def DG_l_(xb, T):
    R = 8.31446261815324
    xa = 1 - xb
    if (T >= 800 and T <= 1200):
        return xb*(12000 - 10*T) + R*T*(xa*np.log(xa) + xb*np.log(xb)) - 20000*xa*xb ###
    elif (T <= 800 and T <= 1200):
        return (12000 - 10*T)*xb + (8000 - 10*T)*xa + R*T*(xa*np.log(xa) + xb*np.log(xb)) - 20000*xa*xb ###
    else:
        return R*T*(xa*np.log(xa) + xb*np.log(xb)) - 20000*xa*xb ###

def d_DG_l_(xb, T):
    R = 8.31446261815324
    xa = 1 - xb
    if (T >= 800 and T <= 1200):
        return 12000 - 10*T - 20000*xa + 20000*xb + R*T*(- np.log(xa) + np.log(xb)) ###
    elif (T <= 800 and T <= 1200):
        return 4000 - 20000*(1-xb) + 20000*xb + R*T*(np.log(xb) - np.log(xa)) ###
    else:
        return R*T*(np.log(xb) - np.log(xa)) - 20000*xa + 20000*xb ###


#-------------------------------------------------------------#
### GIBBS FREE ENERGIES OF MIXING for the SOLID SOLUTIONS ###
#-------------------------------------------------------------#

def DG_s_(xb, T):
    R = 8.31446261815324
    xa = 1 - xb
    if (T >= 800 and T <= 1200):
        return - xa*(8000 - 10*T) + R*T*(xa*np.log(xa) + xb*np.log(xb)) ###
    elif (T <= 800 and T <= 1200):
        return R*T*(xa*np.log(xa) + xb*np.log(xb)) ###
    else:
        return -xa*(8000 - 10*T) - xb*(12000 - 10*T) + R*T*(xa*np.log(xa) + xb*np.log(xb)) ###

def d_DG_s_(xb, T):
    R = 8.31446261815324
    xa = 1 - xb
    if (T >= 800 and T <= 1200):
        return 8000 - 10*T + R*T*(- np.log(xa) + np.log(xb)) ###
```

```
    elif (T <= 800 and T <= 1200):
        return R*T*(np.log(xb) - np.log(xa)) ###
    else:
        return R*T*(np.log(xb) - np.log(xa)) - 4000 ###
```

The tangents are depicted as:

```
    y_tan_l = d_DG_l_(xl0, T) * (xb - xl0) + DG_l_(xl0, T)
        y_tan_s = d_DG_s_(xs0, T) * (xb - xs0) + DG_s_(xs0, T)
```

function

```
    phaseDiagram
```

is to find the common tangent(s), $y_{tan,l} = y_{tan,s}$ at $x_B = 0$. So, let's find some $x_{l,0}$ and $x_{s,0}$ to satisfy that:

```
    d_DG_l_(x1, T) - d_DG_s_(x2, T) = 0
        d_DG_l_(x1, T)*(x1 - x2) - (DG_l_(x1, T) - DG_s_(x2, T)) = 0
```

Get compositions in equilibrium from a given temperature

In [4]:

```
def phaseDiagram(T):
    #y_tan_l = d_DG_l_(xl0, T) * (xb - xl0) + DG_l_(xl0, T)
    #y_tan_s = d_DG_s_(xs0, T) * (xb - xs0) + DG_s_(xs0, T)

    f1  = lambda x:   DG_l_(x, T)
    df1 = lambda x: d_DG_l_(x, T)
    f2  = lambda x:   DG_s_(x, T)
    df2 = lambda x: d_DG_s_(x, T)

    def eqns(x):
        x1, x2 = x[0], x[1]
        eq1 = df1(x1) - df2(x2)
        eq2 = df1(x1)*(x1 - x2) - (f1(x1) - f2(x2))
        return [eq1, eq2]

    from scipy.optimize import least_squares
    lowerbound = 0.0000001
    upperbound = 0.9999999
    lb = (lowerbound, lowerbound) # lower bounds on x1, x2
    ub = (upperbound, upperbound) # upper bounds

    x0 = least_squares(eqns, [0.01, 0.01], bounds=(lb, ub)) # liquid xs
    x1 = least_squares(eqns, [0.99, 0.99], bounds=(lb, ub)) # solid xs

    #print(x0.x, x1.x)
    return x0.x[0], x0.x[1], x1.x[0], x1.x[1]
```

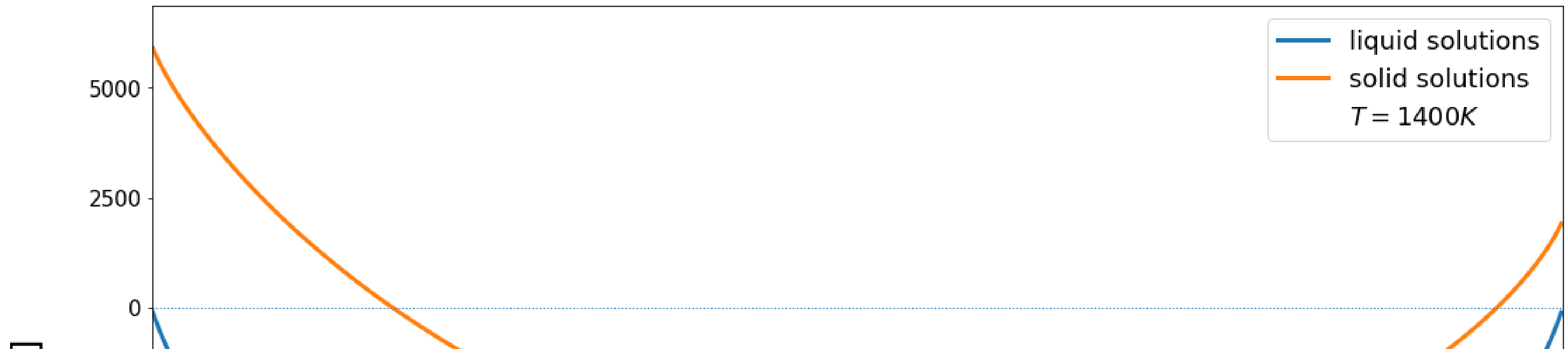
PLOT Gibbs Curves

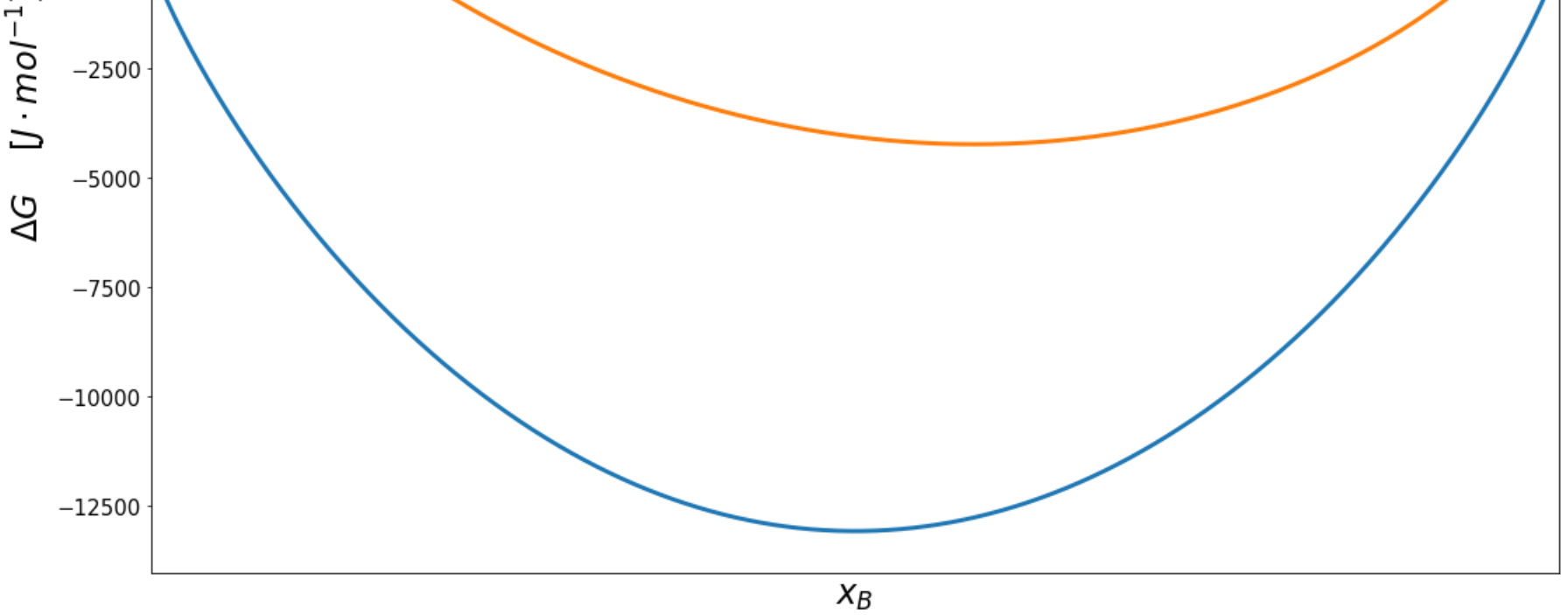
In [5]:

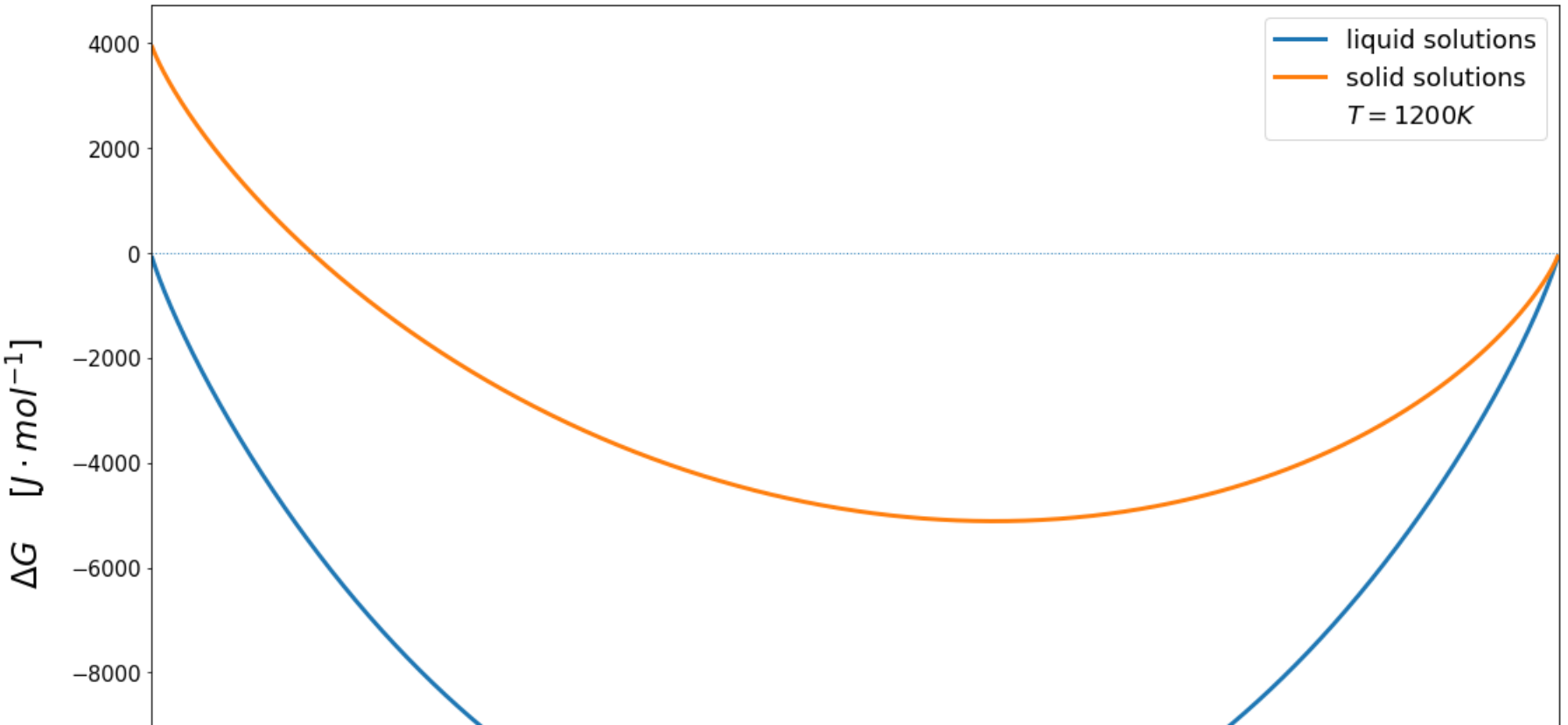
```
def gibbsCurves(T):
    xb = np.linspace(0.0, 1.0, 1000)
    comp = phaseDiagram(T);

    # PLOT FIG
    scale = 6;
    fig, ax = plt.subplots(figsize=(3*scale, 2*scale));

    # Plot
    #plt.scatter(T, C, s=25, color='red', label='Raw data');
    x = xb
    yl = DG_l_(xb, T)
    plt.plot(x, yl, '-', linewidth=3, label='liquid solutions')

    x = xb
    ys = DG_s_(xb, T)
    plt.plot(x, ys, '-', linewidth=3, label='solid solutions')

    # A,}JXJJHYy*pVeM6
    ax.set(autoscale_on=False)
    ax.set_xticks(ax.get_xticks()[::100]) # remove unnecessary ticks
    ax.ticklabel_format(useOffset=False)  # disable scientific notation
    plt.axhline(y=0, linestyle=':', linewidth=1)

    # plot tangents
    lowerbound = 0.0000001
    upperbound = 0.9999999

    if (round(comp[0],3) > lowerbound and round(comp[1],3) < upperbound):
        # plot tangents
        y_tan_l = d_DG_l_(comp[0], T) * (xb - comp[0]) + DG_l_(comp[0], T)
        y_tan_s = d_DG_s_(comp[1], T) * (xb - comp[1]) + DG_s_(comp[1], T)
        if round(y_tan_l[0],2) == round(y_tan_s[0],2):
            plt.plot(x, y_tan_l, '--', linewidth=2)
            #plt.plot(x, y_tan_s, '--', linewidth=2)
            # add values as ticks
            extraticks=[comp[0], comp[1]]
            plt.xticks(list(plt.xticks()[0]) + extraticks)
            plt.axvline(x=comp[0], linestyle=':', linewidth=1)
            plt.axvline(x=comp[1], linestyle=':', linewidth=1)
            # add chemical potentials as legend
            plt.scatter(xb[0], yl[0], s=0, label=r'$\mu_{A,1} = $' + str(round(y_tan_l[0], 2)))
            plt.scatter(xb[0], yl[0], s=0, label=r'$\mu_{B,1} = $' + str(round(y_tan_l[len(y_tan_l)-1], 2)))

    if (round(comp[2],3) > lowerbound and round(comp[3],3) < upperbound):
        # plot tangents
        y_tan_l = d_DG_l_(comp[2], T) * (xb - comp[2]) + DG_l_(comp[2], T)
        y_tan_s = d_DG_s_(comp[3], T) * (xb - comp[3]) + DG_s_(comp[3], T)
        if round(y_tan_l[0],2) == round(y_tan_s[0],2):
            plt.plot(x, y_tan_l, '--', linewidth=2)
            #plt.plot(x, y_tan_s, '--', linewidth=2)
            # add compositions as ticks
            extraticks=[comp[2], comp[3]]
```

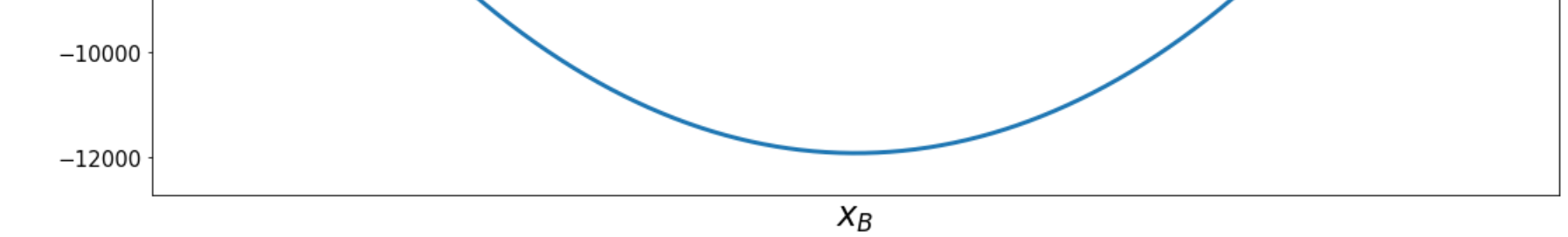
```
            plt.xticks(list(plt.xticks()[0]) + extraticks)
            plt.axvline(x=comp[2], linestyle=':', linewidth=1)
            plt.axvline(x=comp[3], linestyle=':', linewidth=1)
            # add chemical potentials as legend
            plt.scatter(xb[0], yl[0], s=0, label=r'$\mu_{A,2} = $' + str(round(y_tan_l[0], 2)))
            plt.scatter(xb[0], yl[0], s=0, label=r'$\mu_{B,2} = $' + str(round(y_tan_l[len(y_tan_l)-1], 2)))

    # Print fitting parameters as plot legends
    plt.scatter(xb[0], yl[0], s=0, label=r'$T = $' + str(round(T, 2)) + r'$K$')

    # Display plots
    plt.xlim(0.0, 1.0)
    plt.yscale('linear');
    plt.xlabel(r'$x_B$', fontsize=24);
    plt.ylabel(r'$\Delta G$' + '     ' + r'$[J \cdot mol^{-1}]$', fontsize=24);
    #plt.title('Figure 1', size=24);
    plt.legend(prop={'size': 18});
    display(plt);

###############
T = [1400, 1200, 1000, 800, 600, 480, 450]
for t in T:
    gibbsCurves(t)
```

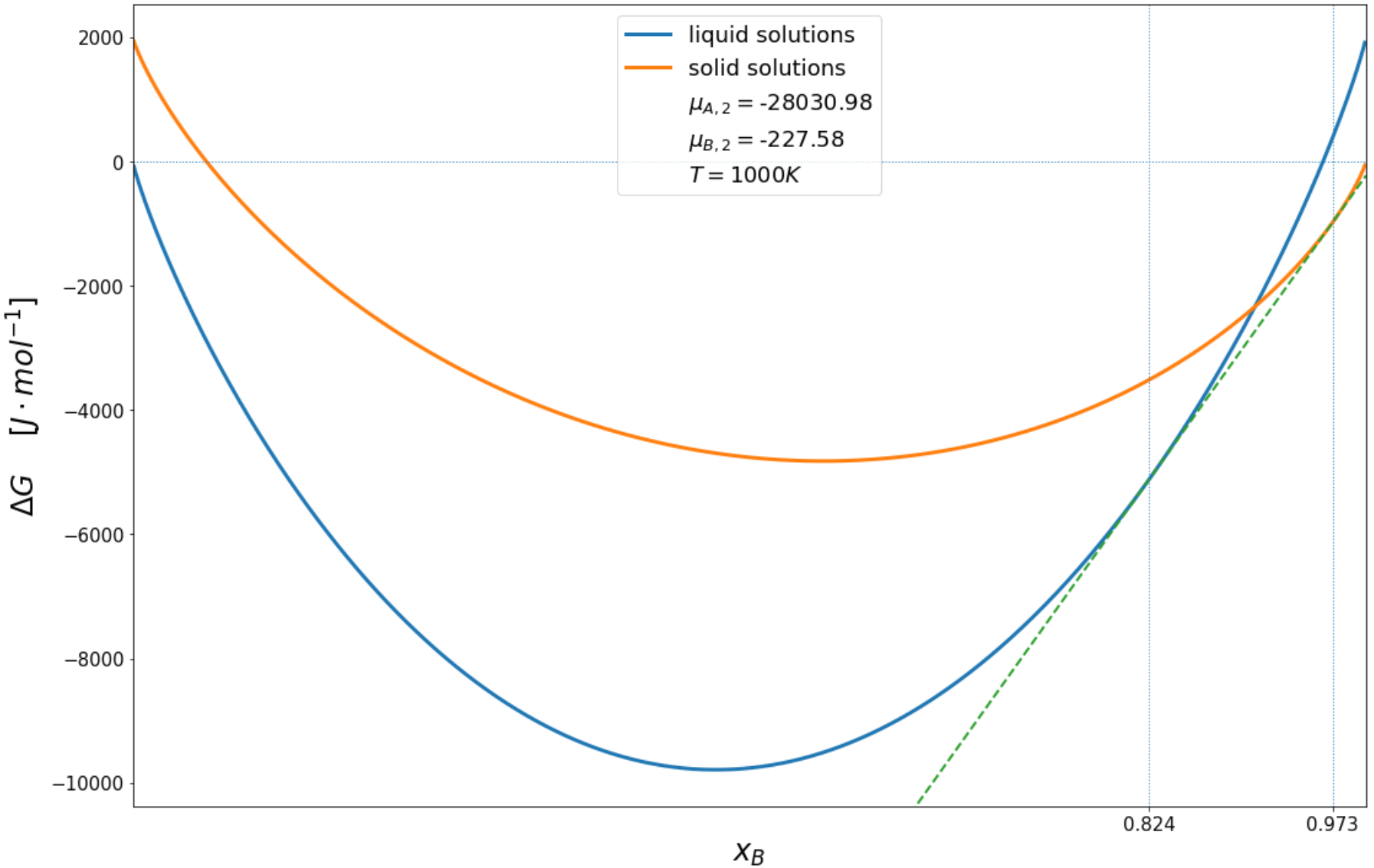
```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>

<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>

<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>

<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>

<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>

<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>

<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>
```



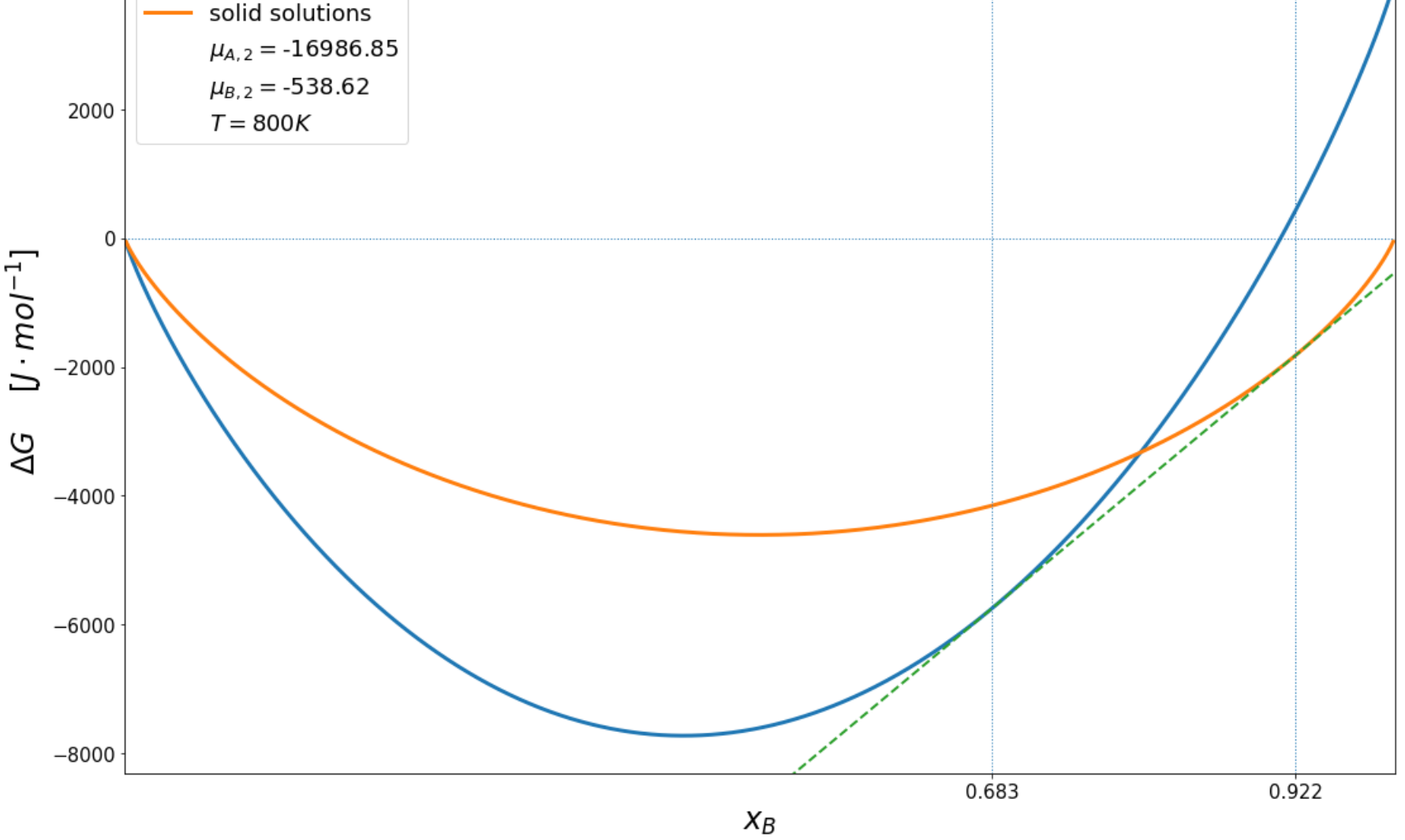

−2500
−5000
−7500
−10000
−12500
$\Delta G \quad [J \cdot mol^{-1}]$
x_B

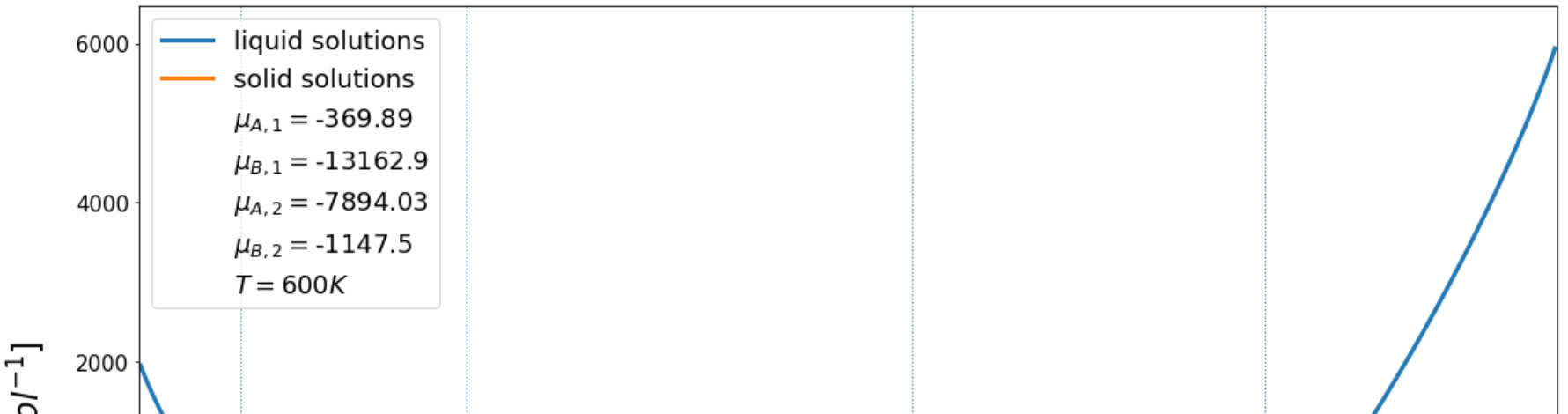

liquid solutions
solid solutions
$T = 1200K$
4000
2000
0
−2000
−4000
−6000
−8000
$\Delta G \quad [J \cdot mol^{-1}]$

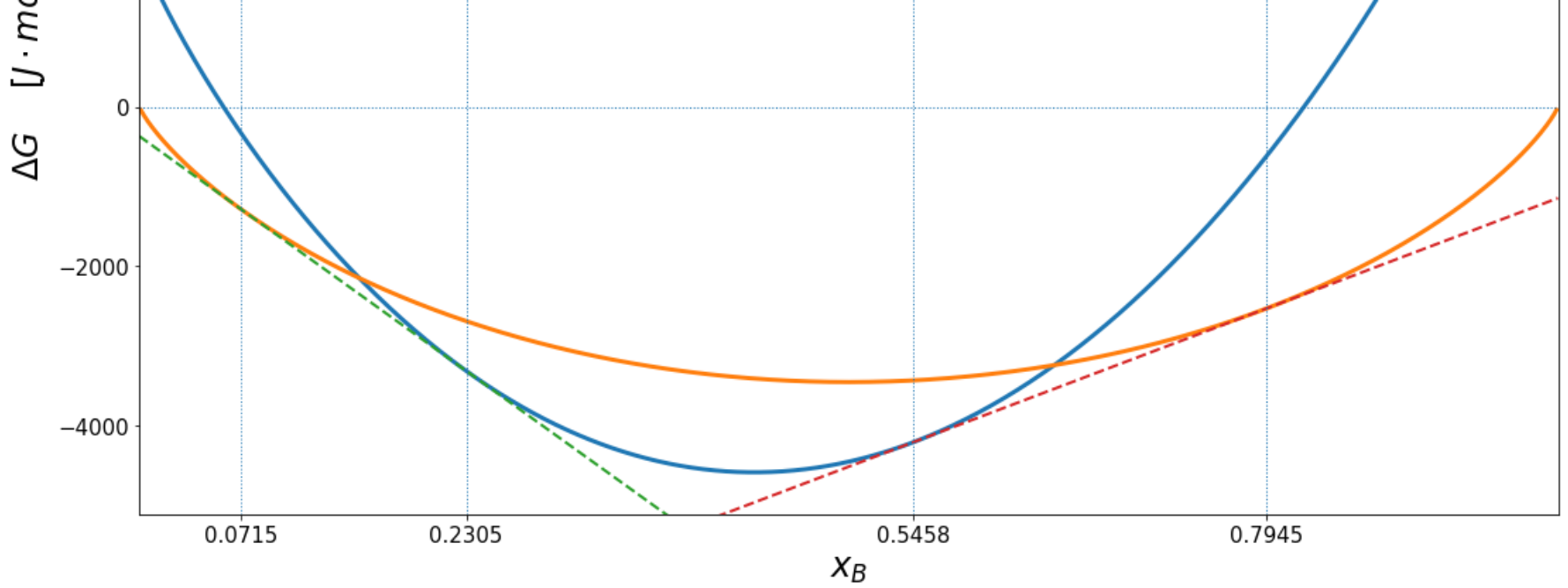

−10000
−12000
x_B

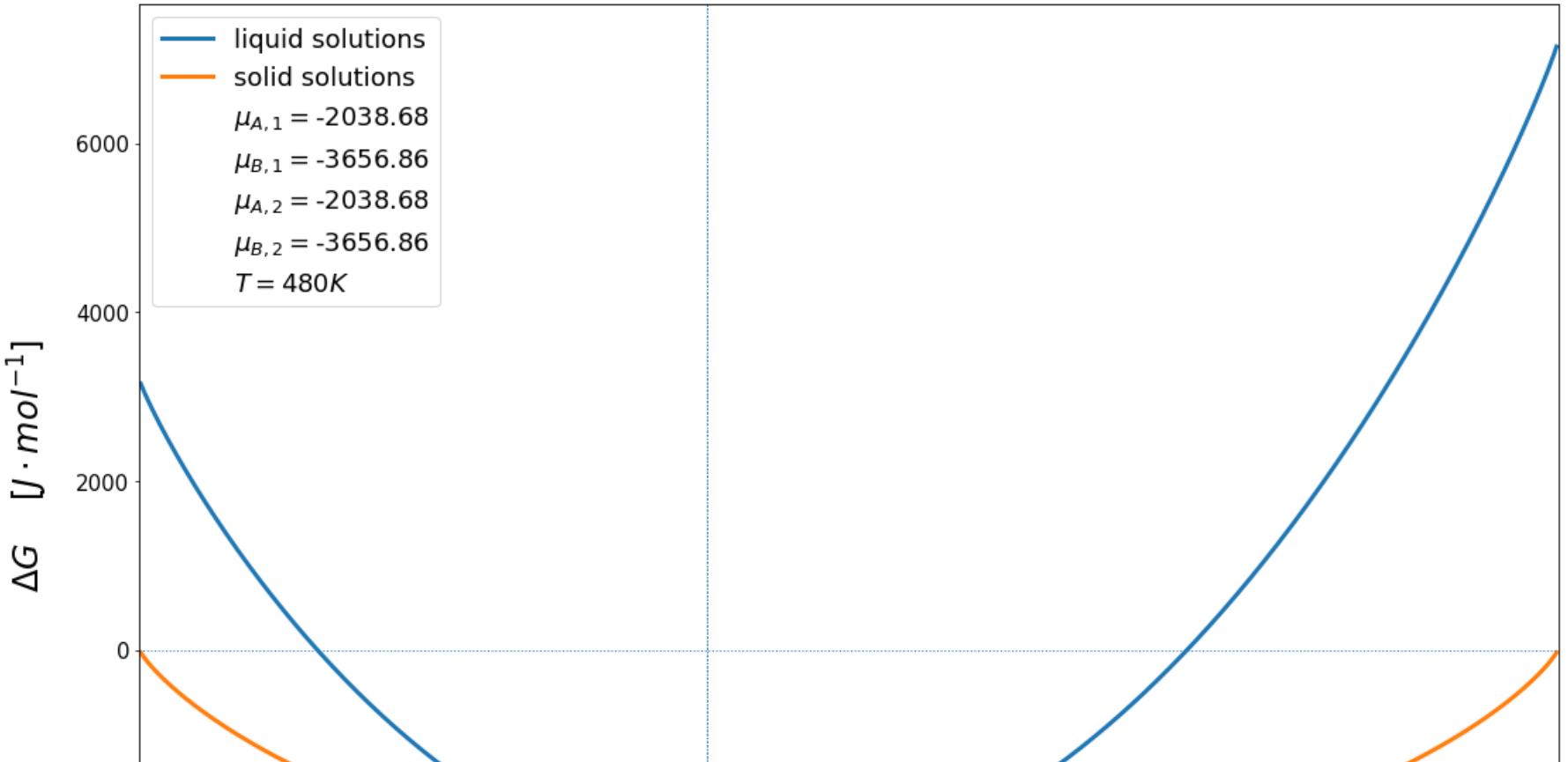

liquid solutions
solid solutions
$\mu_{A,2}$ = -28030.98
$\mu_{B,2}$ = -227.58
$T = 1000K$
2000
0
−2000
−4000
−6000
−8000
−10000
$\Delta G \quad [J \cdot mol^{-1}]$
0.824
0.973
x_B

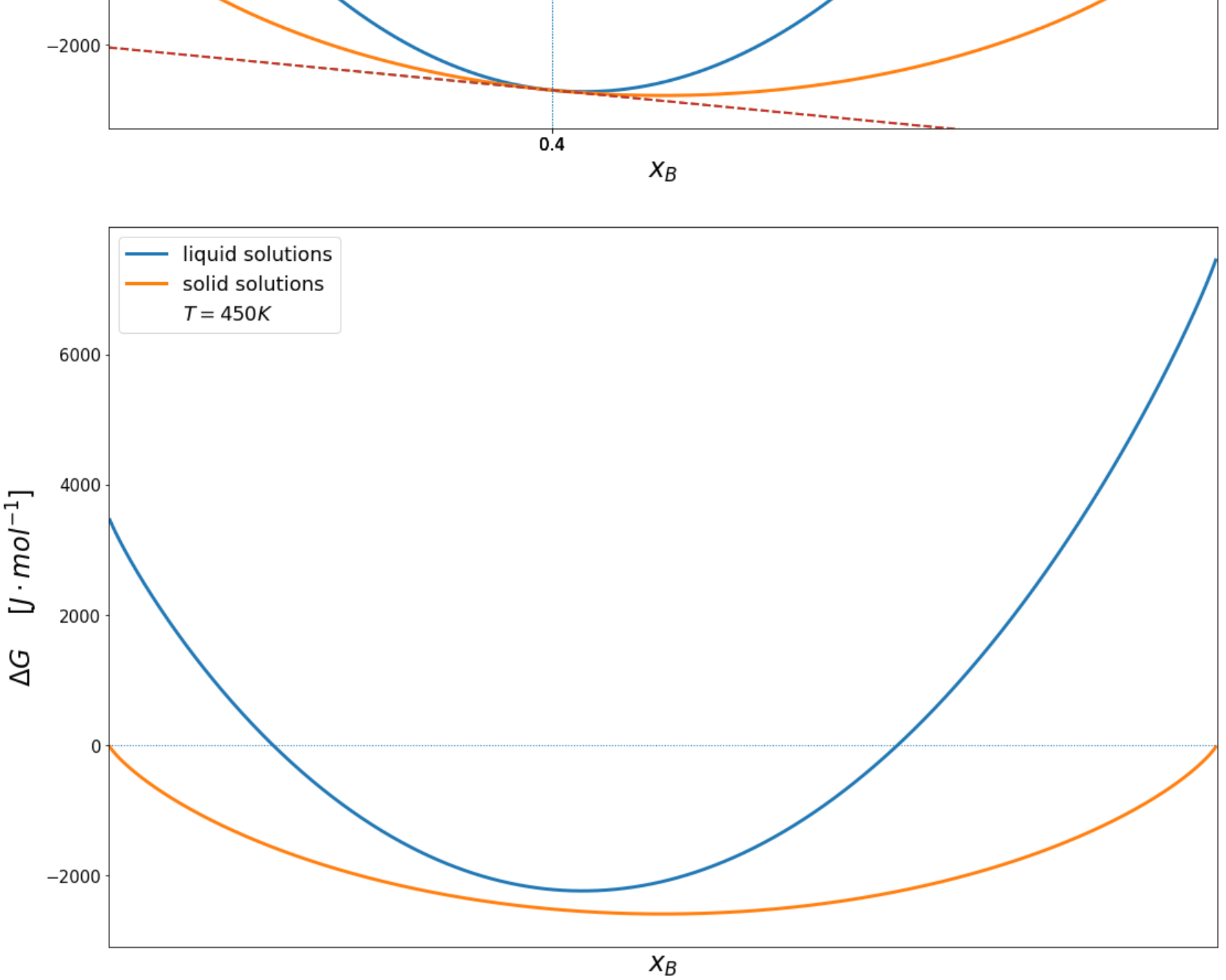

liquid solutions
4000


solid solutions
$\mu_{A,2}$ = -16986.85
$\mu_{B,2}$ = -538.62
$T = 800K$
2000
0
−2000
−4000
−6000
−8000
$\Delta G \quad [J \cdot mol^{-1}]$
0.683
0.922
x_B


liquid solutions
solid solutions
$\mu_{A,1}$ = -369.89
$\mu_{B,1}$ = -13162.9
$\mu_{A,2}$ = -7894.03
$\mu_{B,2}$ = -1147.5
$T = 600K$
6000
4000
2000
$[J \cdot mol^{-1}]$


0
−2000
−4000
0.0715
0.2305
0.5458
0.7945
x_B


liquid solutions
solid solutions
$\mu_{A,1}$ = -2038.68
$\mu_{B,1}$ = -3656.86
$\mu_{A,2}$ = -2038.68
$\mu_{B,2}$ = -3656.86
$T = 480K$
6000
4000
2000
0
$\Delta G \quad [J \cdot mol^{-1}]$

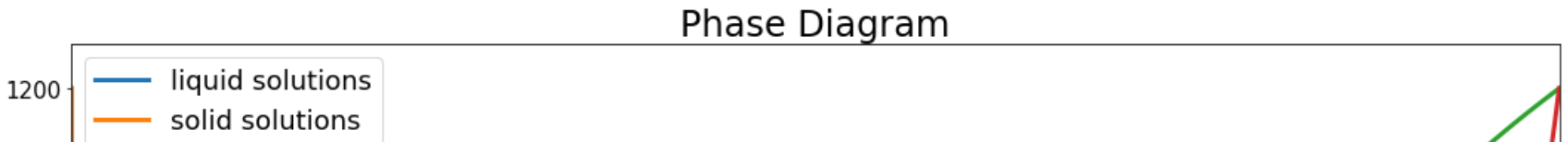


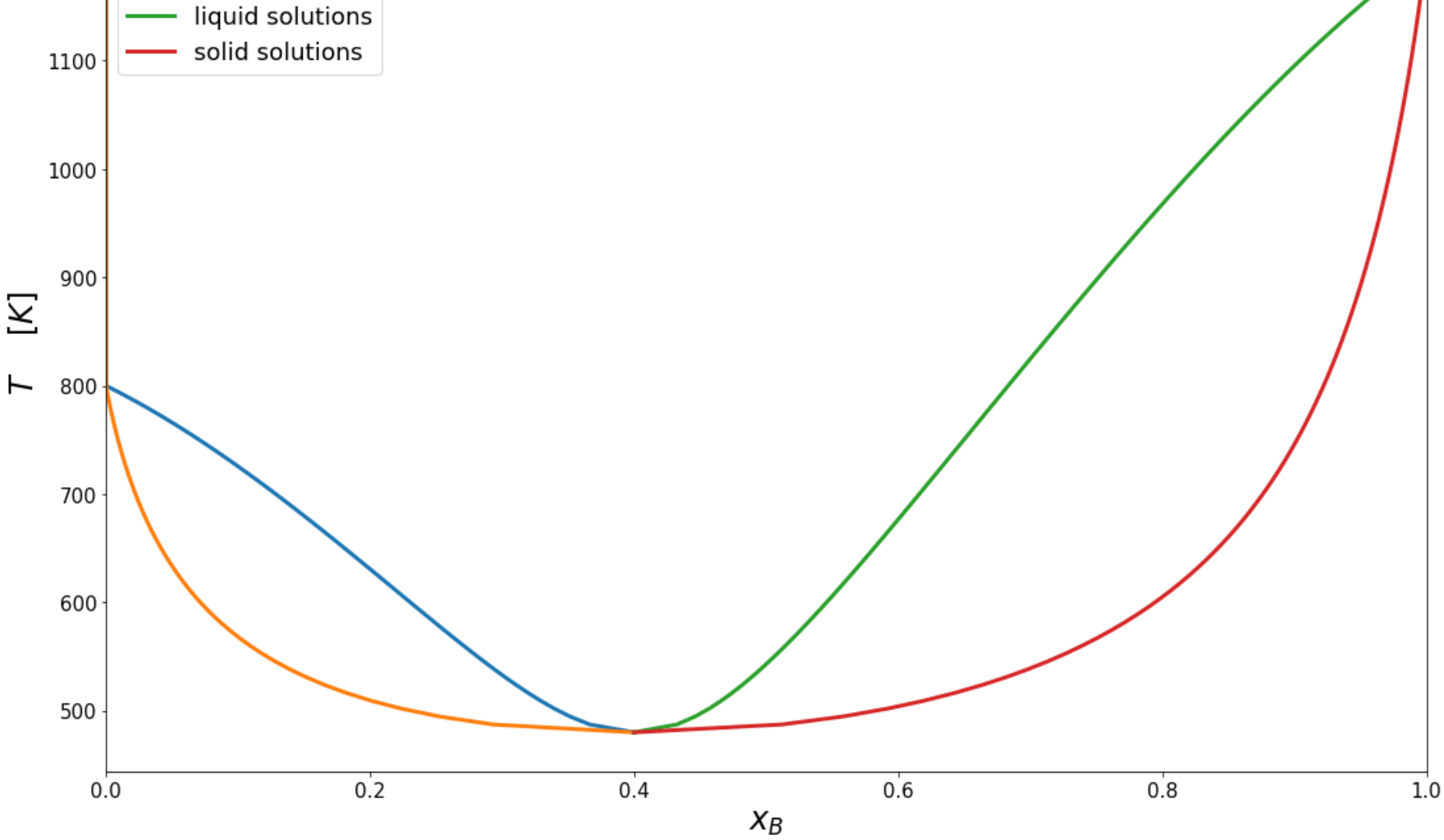
PLOT Phase Diagram

In [6]:

```
T = np.linspace(480.0, 1200.0, 100)
xb = np.linspace(0.0, 1.0, 100)

comp0 = []
comp1 = []
comp2 = []
comp3 = []
for t in T:
    comp = phaseDiagram(t);
    comp0.append(comp[0])
    comp1.append(comp[1])
    comp2.append(comp[2])
    comp3.append(comp[3])

# PLOT FIG
scale = 6;
fig, ax = plt.subplots(figsize=(3*scale, 2*scale));

# Plot
#plt.scatter(T, C, s=25, color='red', label='Raw data');
x = comp0
y = T
plt.plot(x, y, '-', linewidth=3, label='liquid solutions')

x = comp1
y = T
plt.plot(x, y, '-', linewidth=3, label='solid solutions')

x = comp2
y = T
plt.plot(x, y, '-', linewidth=3, label='liquid solutions')

x = comp3
y = T
plt.plot(x, y, '-', linewidth=3, label='solid solutions')

ax.ticklabel_format(useOffset=False)  # disable scientific notation

# Display plots
plt.xlim(0.0, 1.0)
plt.yscale('linear');
plt.xlabel(r'$x_B$', fontsize=24);
plt.ylabel(r'$T$' + '    ' + r'$[K]$', fontsize=24);
plt.title('Phase Diagram', size=24);
plt.legend(prop={'size': 18});
display(plt);
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>
```





As depicted by the reproductions, the Gibbs curves are identical to the ones in Gaskell's book.

However the blue line in the reproduced phase diagram differs from Gaskell's. (Can't explain why ...)

In [7]:

```
import pdfkit
path_wkthmltopdf = r'C:\Program Files\wkhtmltopdf\bin\wkhtmltopdf.exe'
config = pdfkit.configuration(wkhtmltopdf=path_wkthmltopdf)

options = {
    'page-size': 'A4',
    'margin-top': '0.0in',
    'margin-right': '0.0in',
    'margin-bottom': '0.0in',
    'margin-left': '0.0in',
```

```
    'encoding': "UTF-8",
    'custom-header' : [
        ('Accept-Encoding', 'gzip')
    ],
    'cookie': [
        ('cookie-name1', 'cookie-value1'),
        ('cookie-name2', 'cookie-value2'),
    ],
    'no-outline': None,
    'orientation': 'Landscape'
}

pdfkit.from_file('./BinaryPhaseDiagrams.html','BinaryPhaseDiagrams.pdf', configuration=config, options=options)
```

```
Loading pages (1/6)
Warning: Failed to load file:///C:/Users/oskat/OneDrive - Instituto Tecnologico y de Estudios Superiores de Monterrey/Documents/MNT_ITESM_courses/2.2.ThermodynamicsOf
Materials/classActivity03/custom.css (ignore)
Counting pages (2/6)
Resolving links (4/6)
Loading headers and footers (5/6)
Printing pages (6/6)
Done
```

Out[7]:

```
True
```

In [ ]:

```
```