Numerical Analysis For Materials

Mid-term report

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POSTECH

Midterm report 에서 가장 힘들었던 오류

```
double f_1(double T, double x_L, double x_FCC, double x_BCC)
{
    double f_1 = G_Ps_FtoL(T) + R*T*log(1 - x_L) + pow(x_L, 2)*(L_0_L(T) + L_1_L(T) * (2 * x_L - 1))
        - (R*T*log(1 - x_FCC) + pow(x_FCC, 2)*(L_0_L(T) + L_1_FCC(T) * (2 * x_FCC - 1)));
```

L_0_FCC를 L_0_L로 써서 못 찾고 4시간 날렸습니다…
한동안 코딩을 못 잡겠더라구요…

Mid-term report

Phase diagram of Ps-Tk

POSTECH

1. Defining the question

Q) Postechium (Ps)과 Tohokium(Tk) 2 원계에 대한 실험 정보는 다음과 같이 발표되어있다. 이를 바탕으로 **Liquid, fcc, bcc 각 상에 대한 열역학 수식화**를 수행하고 **Ps-Tk 2 원계 상태도**를 계산하시오.

Experimental data)

- $\Delta^{\circ}G_{Ps}^{fcc\rightarrow liquid} = 15000 - 12T$
- $\Delta^{\circ}G_{Ps}^{fcc\rightarrow liquid} = 6000 - 10T$
- $\Delta^{\circ}G_{Ps}^{fcc\rightarrow liquid} = 4000$
- $\Delta^{\circ}G_{Ps}^{fcc\rightarrow liquid} = 7500$
- 액상에서의 Enthalpy of mixing (J/mol)
- 1500 K 액상에서 Tk 의 활동도 (reference state: Liquid Tk)
- Enthalpy of Formation in FCC and BCC
- Activity of Ps in BCC and Activity of Tk in FCC at 600 K

2. Idea to construct phase diagram

1) 주어진 각 data에 대한 관계식의 선형화

For sub-regular solution: $\boldsymbol{\Omega} = L_0 + L_1 X_{Tk} + L_2 X_{Tk}^2 + L_3 X_{Tk}^3 \cong \boldsymbol{L_0} + \boldsymbol{L_1 X_{Tk}}$
(from Thermodynamics of D. R. Gaskell)

2) Regression을 통해 각 phase에 대한 $\boldsymbol{L_0}$, $\boldsymbol{L_1}$ 값 구하기(각 상수는 T에 대한 일차 식으로 표현)

L, FCC, BCC phase 각각이 어떤 model인지도 결정

3) Gibbs free energy, Chemical potential equation 재 정리

4) Eq. condition으로부터 non-linear eq. 풀기 -> Phase diagram 도시

3. Results

1) 주어진 각 data에 대한 관계식의 선형화 (HW#6)

For sub-regular solution: $\boldsymbol{\Omega} = L_0 + L_1 X_{Tk} + L_2 X_{Tk}^2 + L_3 X_{Tk}^3 \cong \boldsymbol{L_0} + \boldsymbol{L_1 X_{Tk}}$

(from Thermodynamics of D. R. Gaskell)

(Liquid) Enthalpy of mixing:

$$\frac{\Delta H^M}{X_{Tk}(1 - X_{Tk})} = (\boldsymbol{L_0} + \boldsymbol{L_1} X_{Tk})$$

(Liquid) Activity of Tk:

$$\frac{RT\ln a_{Tk} - RT\ln X_{Tk}}{(1 - X_{Tk})^2} = \boldsymbol{L_0} + \boldsymbol{L_1}(2X_{Tk})$$

(FCC) Enthalpy of Formation:

$$\frac{\Delta H_f^{FCC} - 7500 X_{Tk}}{X_{Tk}(1 - X_{Tk})} = (\boldsymbol{L_0} + \boldsymbol{L_1} X_{Tk})$$

(FCC) Activity of Tk:

$$\frac{RT\ln a_{Tk} - RT\ln X_{Tk} - 7500}{(1 - X_{Tk})^2} = \boldsymbol{L_0} + \boldsymbol{L_1}(2X_{Tk})$$

(BCC) Enthalpy of Formation:

$$\frac{\Delta H_f^{BCC} - 4000(1 - X_{Tk})}{X_{Tk}(1 - X_{Tk})} = (\boldsymbol{L_0} + \boldsymbol{L_1}(1 - X_{Tk}))$$

(BCC) Activity of Ps:

$$\frac{RT\ln a_{Ps} - RT\ln(1 - X_{Tk}) - 4000}{(X_{Tk})^2} = \boldsymbol{L_0} + \boldsymbol{L_1}(2(1 - X_{Tk}))$$

3. Results

2) Regression을 통해 각 phase에 대한 L_0, L_1 값 구하기(HW#6)

```
C:₩Windows₩system32₩cmd.exe
==============================================================================
Program: Regression of Ps-Tk data
Date: 2015.04.21
Made by Gilwoon Lee
POSTECH, project 6 of [AMSE417] Numerical analysis for materials
Development environment: Visual Studio 2013
Code language: C
==============================================================================

This programm will do Regression of Ps-Tk data.
============================

* Enter file name(*.txt): enthalpy_mix.txt
# of data: 39
L_0: 14894.230619
L_1: -4794.925467
r^2: 0.999997
Enter 1 to repeat, 0 to exit: 1

* Enter file name(*.txt): activity_1500_Tk.txt
# of data: 39
L_0: 2907.166476
L_1: -4811.777322
r^2: 0.999975
Enter 1 to repeat, 0 to exit: 1

* Enter file name(*.txt): enthalpy_form_FCC.txt
# of data: 20
L_0: 12597.609462
L_1: -7199.977924
r^2: 0.999997
Enter 1 to repeat, 0 to exit: 1
```

```
* Enter file name(*.txt): enthalpy_form_BCC.txt
# of data: 16
L_0: 7000.661574
L_1: -1.638188
r^2: 0.007057
Enter 1 to repeat, 0 to exit: 1

* Enter file name(*.txt): activity_600_Tk.txt
# of data: 20
L_0: 9596.838369
L_1: -7192.026746
r^2: 0.999994
Enter 1 to repeat, 0 to exit: 1

* Enter file name(*.txt): activity_600_Ps.txt
# of data: 16
L_0: 4566.182191
L_1: 42.653319
r^2: 0.138815
Enter 1 to repeat, 0 to exit: 0

============================
계속하려면 아무 키나 누르십시오 . . .
```

Meaningless

Meaningless

3. Results

2) Regression을 통해 각 phase에 대한 L_0, L_1 값 구하기(HW#6+추가)

(Liquid) T=1500 K

$$L_{0,\,liq} = 14894.230619 - L_{sub,\,0,\,liq}T = 2907.166476$$
$$L_{1,\,liq} = -4794.925467 - L_{sub,\,1,\,liq}T = -4811.777322$$

▼

Sub-regular: $\boldsymbol{\Omega} = (\mathbf{14894.230619} - \mathbf{7.991376}\boldsymbol{T}) + (-\mathbf{4794.925467} - \mathbf{0.011235}\boldsymbol{T})\boldsymbol{X_{Tk}}$

```
* Enter file name(*.txt): enthalpy_mix.txt
# of data: 39
L_0: 14894.230619
L_1: -4794.925467
r^2: 0.999997
Enter 1 to repeat, 0 to exit: 1

* Enter file name(*.txt): activity_1500_Tk.txt
# of data: 39
L_0: 2907.166476
L_1: -4811.777322
r^2: 0.999975
Enter 1 to repeat, 0 to exit: 1
```

(FCC) T=600 K

$$L_{0,\,FCC} = 12597.609462 - L_{sub,\,0,\,FCC}T = 9596.838369$$
$$L_{1,\,FCC} = -7199.977924 - L_{sub,\,1,\,FCC}T = -7192.026746$$

▼

Sub-regular: $\boldsymbol{\Omega} = (\mathbf{12597.609462} - \mathbf{5.001285}\boldsymbol{T}) + (-\mathbf{7199.977924} + \mathbf{0.012352}\boldsymbol{T})\boldsymbol{X_{Tk}}$

```
* Enter file name(*.txt): enthalpy_form_FCC.txt
# of data: 20
L_0: 12597.609462
L_1: -7199.977924
r^2: 0.999997
Enter 1 to repeat, 0 to exit: 1
* Enter file name(*.txt): activity_600_Tk.txt
# of data: 20
L_0: 9596.838369
L_1: -7192.026746
r^2: 0.999994
```

(BCC) T=600 K

$$L_{0,\,BCC} = 7000.661574 - L_{sub,\,0,\,BCC}T = 4566.182191$$
$$L_{1,\,BCC} = 0$$

▼

Regular: $\boldsymbol{\Omega} = \mathbf{7000.661574} - \mathbf{4.057466}\boldsymbol{T}$

```
* Enter file name(*.txt): enthalpy_form_BCC.txt
# of data: 16
L_0: 7000.661574
L_1: -1.636188
r^2: 0.007057
Enter 1 to repeat, 0 to exit: 1
* Enter file name(*.txt): activity_600_Ps.txt
# of data: 16
L_0: 4566.182191
L_1: 42.953319
r^2: 0.138815
Enter 1 to repeat, 0 to exit: 0
```

Meaningless

Meaningless

3. Results

2) Regression을 통해 각 phase에 대한 L_0, L_1 값 구하기(HW#6+추가)

(Liquid) T=1500 K

Sub-regular: $\Omega = (14894.230619 - 7.991376T) + (-4794.925467 - 0.011235T)X_{Tk}$

(FCC) T=600 K

Sub-regular: $\Omega = (12597.609462 - 5.001285T) + (-7199.977924 + 0.012352T)X_{Tk}$

(BCC) T=600 K

Regular: $\Omega = 7000.661574 - 4.057466T$

HW #6 – Results

1. For Liquid and FCC phase, it's sub-regular solution. For BCC phase, it's regular solution.
2. Regression by least square method fits very well!
3. Ω(Liquid)= (14894.7230 – 7.992T) + (–4794.925 – 0.0112T)*X(Tk)
4. Ω(FCC)= (112597.609 – 5.001T) + (–7199.978– 0.0133T)*X(Tk)
5. Ω(BCC) = 7000.31 – 4.00*T

김동훈 선배 결과

4 HW 6 Results – Liquid phase

```
[Enthalpy of Mixing]
L0= 14894.230619
L1= -4794.925467
r2= 0.9999971320

[Activity of Tk at 1500K]
L0= 2907.169938
L1= -9623.566102
r2= 0.9999746051
```

→ 실제로는 2L1값!
L1= -4811.783051

두 경우가 서로 L0, L1이 다르기 때문에
Temperature dependence가 있음을 알 수 있음

$L_0 = L_{01} + L_{02}T$

$L_1 = L_{11} + L_{12}T$

$\Omega = L_0 + L_1 X_{Tk} = (L_{01} + L_{02}T) + (L_{11} + L_{12}T) = (L_{01} + L_{11}) + (L_{02} + L_{12})T$

각각 대입해서 계산해보면

$\Omega = (14894.23 - 7.99T) + (-4794.93 - 0.0112T)X_{Tk}$

4 HW 6 Results – FCC

```
[Enthalpy of Formation in FCC]
L0= 12597.609462
L1= -7199.977924
r2= 0.9999974319

[Activity of Tk in FCC at 600K]
L0= 9596.854839
L1= -14384.019210
r2= 0.9999940732
```

→ 실제로는 2L1값!
L1= -7192.009605

Not equal !
Temperature dependence !!

$\Omega = (12597.61 - 5.00126T) + (-7199.978 - 0.01328T)X_{Tk}$

4 HW 6 Results – BCC

```
[Enthalpy of Formation in BCC]
L0= 7000.661574
L1= -1.638188
r2= 0.0070565234

[Activity of Ps in BCC at 600K]
L0= 4566.191344
L1= 85.727870
r2= 0.1388748657
```

?

Not equal !
Temperature dependence !!
Not sub-regular model

$\Omega = (7000.6616 - 4.05745T)$

조규봉 선배 결과

3. Results

3) Chemical potential equation 재 정리

Reference state: Ps(FCC), Tk(BCC)

(Liquid) **Tk:** $\mu_{Tk}^{L} = \Delta G_{Tk}^{BCC\to L} + RT\ln X_{Tk} + (1 - X_{Tk})^2(L_0^L + 2L_1^L X_{Tk})$

Ps: $\mu_{Ps}^{L} = \Delta G_{Ps}^{FCC\to L} + RT\ln(1 - X_{Tk}) + {X_{Tk}}^2(L_0^L + L_1^L(2X_{Tk} - 1))$

(FCC) **Tk:** $\mu_{Tk}^{FCC} = \Delta G_{Tk}^{BCC\to FCC} + RT\ln X_{Tk} + (1 - X_{Tk})^2\left(L_0^{FCC} + 2L_1^{FCC} X_{Tk}\right)$

Ps: $\mu_{Ps}^{FCC} = RT\ln(1 - X_{Tk}) + {X_{Tk}}^2\left(L_0^{FCC} + L_1^{FCC}(2X_{Tk} - 1)\right)$

(BCC) **Tk:** $\mu_{Tk}^{BCC} = RT\ln X_{Tk} + (1 - X_{Tk})^2\left(L_0^{BCC}\right)$

Ps: $\mu_{Ps}^{BCC} = \Delta G_{Ps}^{FCC\to BCC} + RT\ln(1 - X_{Tk}) + {X_{Tk}}^2\left(L_0^{BCC}\right)$

3. Results

4) Eq. condition으로부터 non-linear eq. 풀기 -> Phase diagram 도시

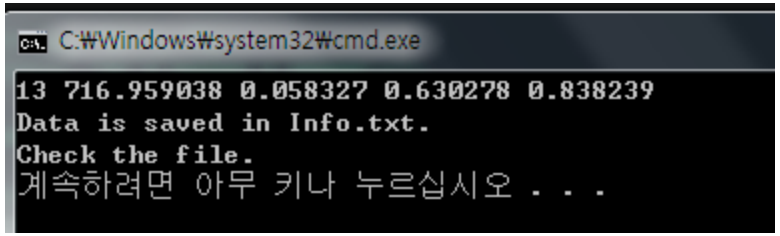
$$\mu_{Tk}^{L} = \mu_{Tk}^{FCC}$$
$$\mu_{Ps}^{L} = \mu_{Ps}^{FCC}$$

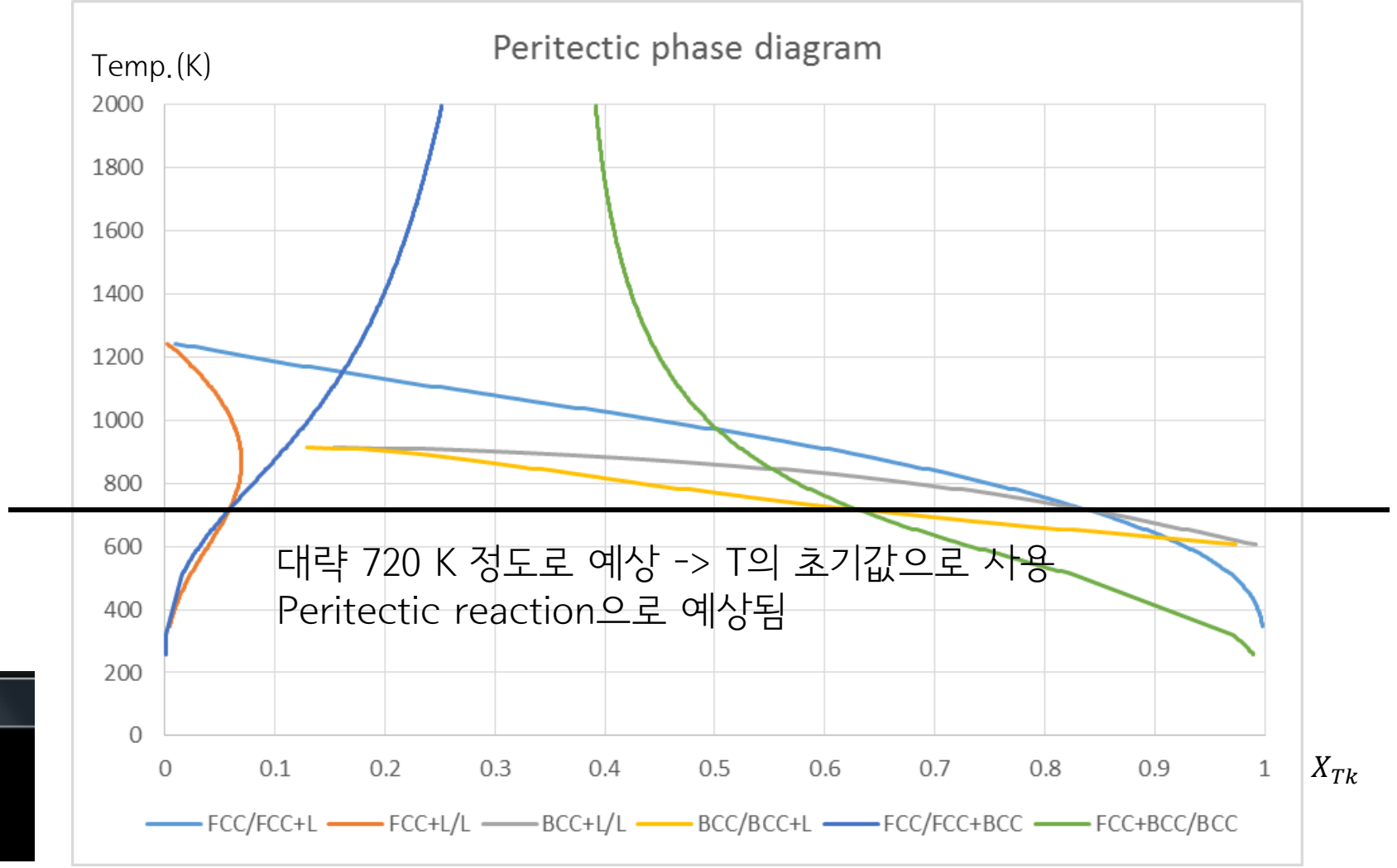
$$\mu_{Tk}^{L} = \mu_{Tk}^{BCC}$$
$$\mu_{Ps}^{L} = \mu_{Ps}^{BCC}$$

$$\mu_{Tk}^{FCC} = \mu_{Tk}^{BCC}$$
$$\mu_{Ps}^{BCC} = \mu_{Ps}^{BCC}$$

$$\mu_{Tk}^{L} = \mu_{Tk}^{FCC} = \mu_{Tk}^{BCC}$$
$$\mu_{Ps}^{L} = \mu_{Ps}^{FCC} = \mu_{Ps}^{BCC}$$

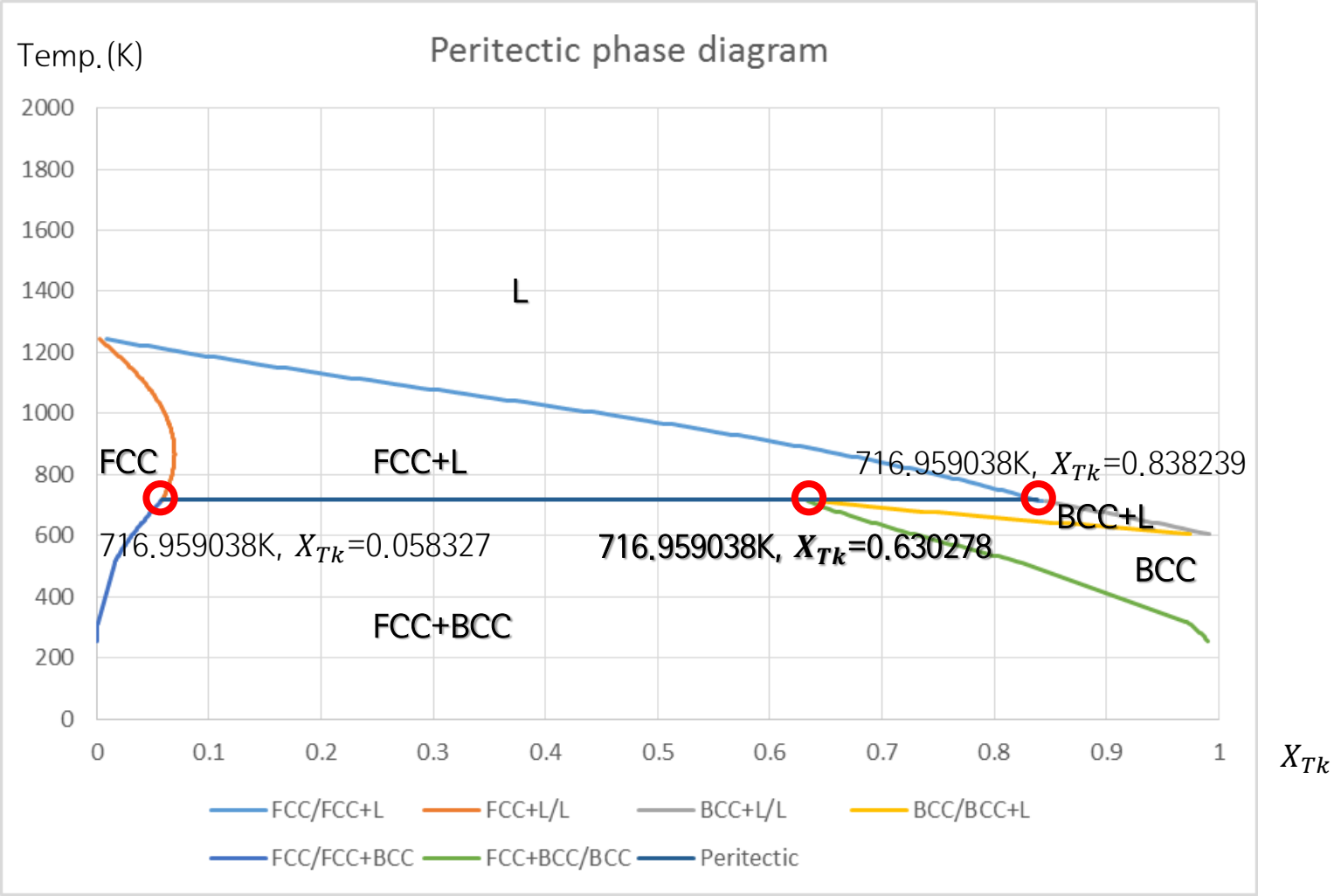
-> Jacobian, Non-linear eq.





3. Results

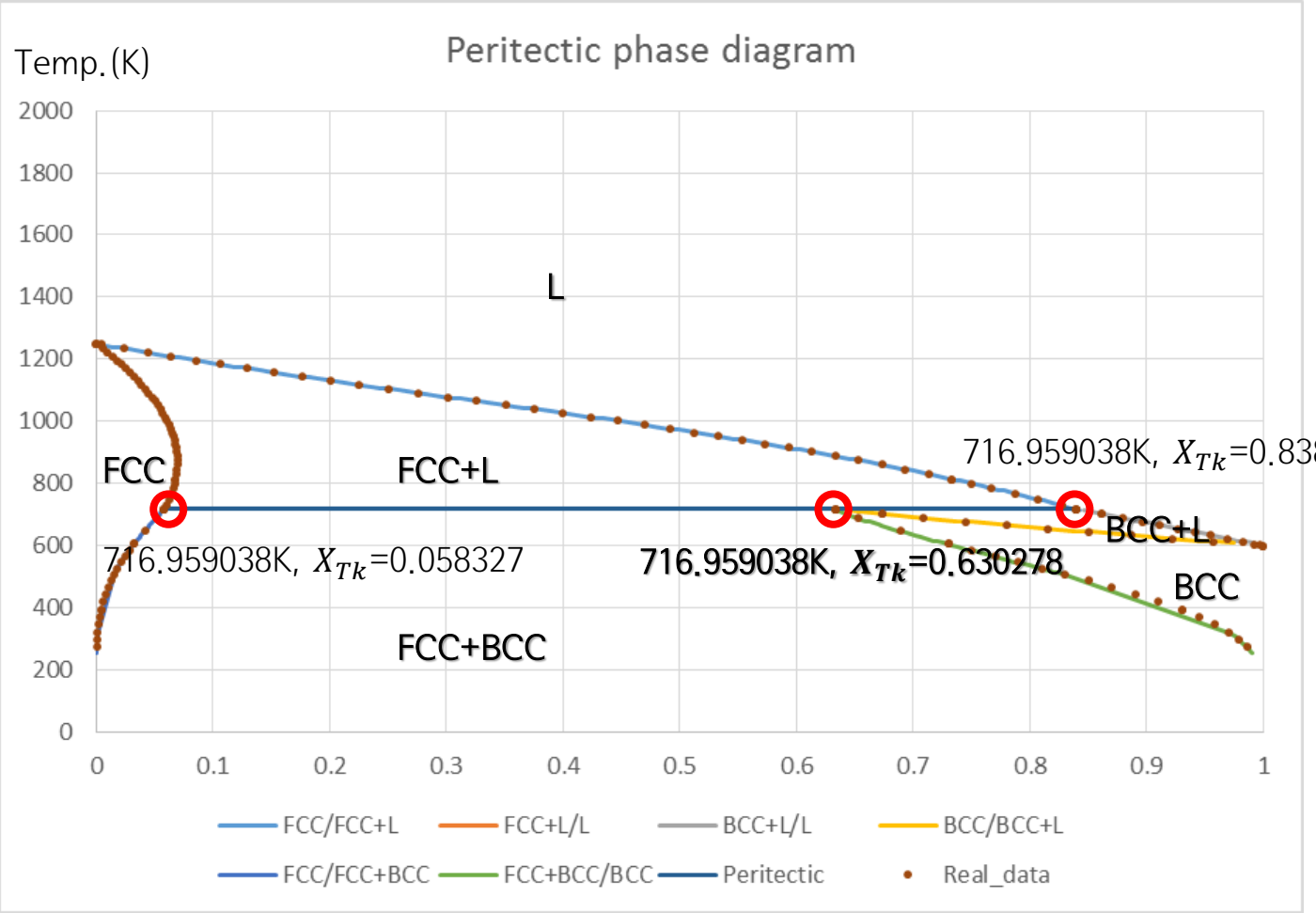
4) Eq. condition으로부터 non-linear eq. 풀기 -> Phase diagram 도시



3. Results

4) Eq. condition으로부터 non-linear eq. 풀기 -> Phase diagram 도시

실제 데이터와의 비교



Peritectic Point

4.4205282593E+02 K
+ 273.15 K
= 7.1520282593E+02 K

Peritectic Temp. 상대오차: 0.24555 %

4. Conclusion

1) 첨자를 사용할 때는 잘 사용해야 한다는 점을 알 수 있었다.
2) 4 by 4를 구할 때 초기값에 민감하게 반응하여 초기값을 잘 선택하는 과정이 필요했다.
3) 주어진 열역학적 데이터를 이용하여 Phase diagram을 성공적으로 그릴 수 있었다!!
   (Peritectic temp. 상대오차 0.24555 %)