Numerical Method

Dept. Material Science & Engineering
Undergraduate Course (4th year)
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Midterm

Regression -> Non-linear Equation System

Data

- Gibbs Energy in pure Ps, Ks
- Enthalpy of Mixing in Liquid
- Activity of Ks in 1500K, Liquid
- Enthalpy of Formation in FCC, BCC
- Activity of Ps in BCC in 1100K
- Activity of Ks in FCC in 1100K

Equation System

- $\mu_L = \mu_{FCC}$
- $\mu_{FCC} = \mu_{BCC}$
- $\mu_L = \mu_{BCC}$
- Change of Temperature
- Binary System

Phase Diagram

Value of L_0, L_1

Temperature-dependent
Sub-regular Solution

Chemical Potential

- Liquid, FCC, BCC Phase
- Ps, Ks

Equation System

- X_L, X_{FCC}, X_{BCC}, Temperature
- $\mu_L = \mu_{FCC} = \mu_{BCC}$ of Ps, Ks
- "Triple Point"

Midterm

Thermodynamics

Enthalpy of Mixing

$$\Delta H_m = \Omega X_{Ps} X_{Ks}$$
$$= L X_{Ps} X_{Ks} \quad \text{(Regular)}$$
$$= (L_0 + L_1 X_{Ks}) X_{Ps} X_{Ks} \quad \text{(Sub-regular)}$$

$$L_0 = L_0^0 + L_0' T \qquad L_1 = L_1^0 + L_1^1 T$$

Liquid Phase

- Enthalpy of Mixing

$$\frac{\Delta H_m^L}{X_{Ks}(1 - X_{Ks})} = L_0^0 + L_1^0 X_{Ks}$$

- Activity of Ks in Liquid

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

FCC Phase

- Enthalpy of Formation

$$\frac{\Delta H_f^{FCC} - \Delta G_{Ks}^{BCC \to FCC} X_{Ks}}{X_{Ks}(1 - X_{Ks})} = L_0^0 + L_1^0 X_{Ks}$$

- Activity of Ks in Liquid

$$\frac{RT(\ln a_{Ks} - \ln X_{Ks}) - \Delta G_{Ks}^{BCC \to FCC}}{(1 - X_{Ks})^2} = L_0 + L_1 (2X_{Ks})$$

BCC Phase

- Enthalpy of Formation

$$\frac{\Delta H_f^{BCC} - \Delta G_{Ps}^{FCC \to BCC} (1 - X_{Ks})}{X_{Ks}(1 - X_{Ks})} = L_0^0 + L_1^0 (1 - X_{Ks})$$

- Activity of Ps in BCC

$$\frac{RT(\ln a_{Ks} - \ln(1 - X_{Ks})) - \Delta G_{Ps}^{FCC \to BCC}}{(X_{Ks})^2} = L_0 + L_1 (2(1 - X_{Ks}))$$

Midterm

Regression

```
Enthalpy of Mixing

 Y = (14894.230619) + (-4794.925467)x
L_0 : 14894.230619
L_1 : -4794.925467
Sum of Square : 203.587186
Value of R : 1.000000

Activity of Ks in liquid (1500K)

 Y = (2907.183224) + (-9623.610085)x
L_0 : 2907.183224
2L_1 : -9623.610085
Sum of Square : 7261.723440
Value of R : 0.999983

Enthalpy of formation in FCC

 Y = (12597.609462) + (-7199.977924)x
L_0 : 12597.609462
L_1 : -7199.977924
Sum of Square : 55.331968
Value of R : 1.000000
```

```
Activity of Ks in fcc (1100K)

 Y = (7100.938341) + (-14350.309179)x
L_0 : 7100.938341
2L_1 : -14350.309179
Sum of Square : 8305.546419
Value of R : 0.999973

Enthalpy of formation in BCC

 Y = (7000.896856) + (-6.654231)x
L_0 : 7000.896856
L_1 : -6.654231
Sum of Square : 94.573085
Value of R : 0.999155

Activity of Ps in BCC (1100K)

 Y = (2688.598526) + (-155.708176)x
L_0 : 2688.598526
2L_1 : -155.708176
Sum of Square : 40726.904212
Value of R : 0.008030
```

Liquid Phase

- 14894.2 - 7.99137T + (-4794.9-0.0112334T) X

FCC Phase

- 12597.6 − 4.99703T+ (−7199.98+0.0224905T)X

BCC Phase

- Sub-regular model -> X
- Regular Model
- 7000.89 − 6.65423T

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Chemical Potential

Reference State : Ks -> BCC
Ps -> FCC

Liquid Phase

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

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

FCC Phase

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

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

BCC Phase

$$\mu_{Ks}^{BCC} = RT\ln X_{Ks} + (1-X_{Ks})^2\left(L_0^{BCC} + 2X_{Ks}L_1^{BCC}\right)$$

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

Liquid - FCC

$$\mu_{Ks}^{L} - \mu_{Ks}^{FCC} = 0$$

$$\mu_{Ps}^{L} - \mu_{Ps}^{FCC} = 0$$

FCC - BCC

$$\mu_{Ks}^{FCC} - \mu_{Ks}^{BCC} = 0$$

$$\mu_{Ks}^{FCC} - \mu_{Ks}^{BCC} = 0$$

Liquid - BCC

$$\mu_{Ks}^{L} - \mu_{Ks}^{BCC} = 0$$

$$\mu_{Ps}^{L} - \mu_{Ps}^{BCC} = 0$$

→ Newton's Method

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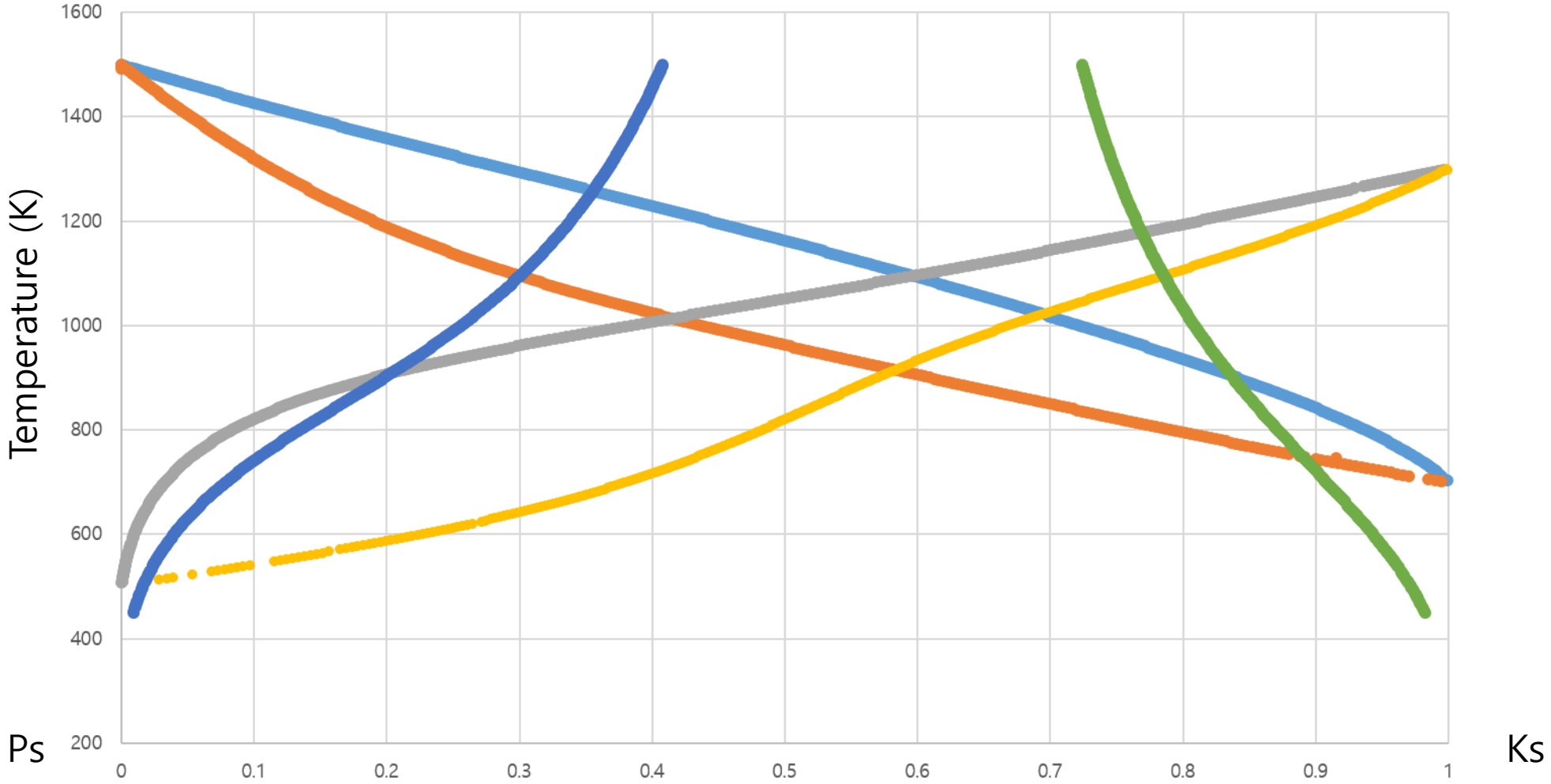
Phase Diagram

(Interval : 2K)



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Chemical Potential

Triple Point

$$\mu_{Ks}^{L} = \mu_{Ks}^{FCC} = \mu_{Ks}^{BCC}$$

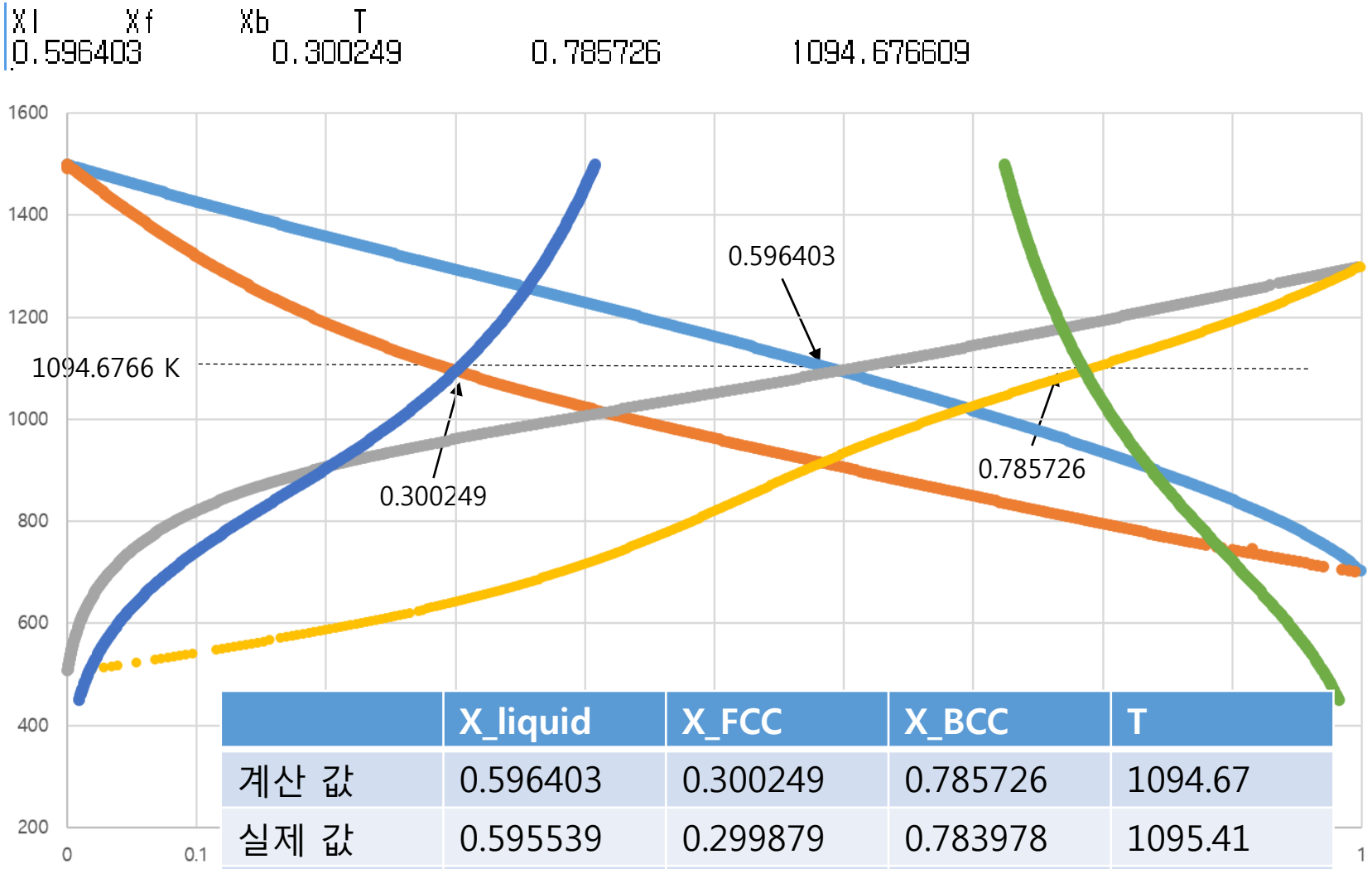
$$\mu_{Ps}^{L} = \mu_{Ps}^{FCC} = \mu_{Ps}^{BCC}$$

$$\mu_{Ks}^{L} - \mu_{Ks}^{FCC} = 0$$

$$\mu_{Ks}^{L} - \mu_{Ks}^{BCC} = 0$$

$$\mu_{Ps}^{L} - \mu_{Ps}^{FCC} = 0$$

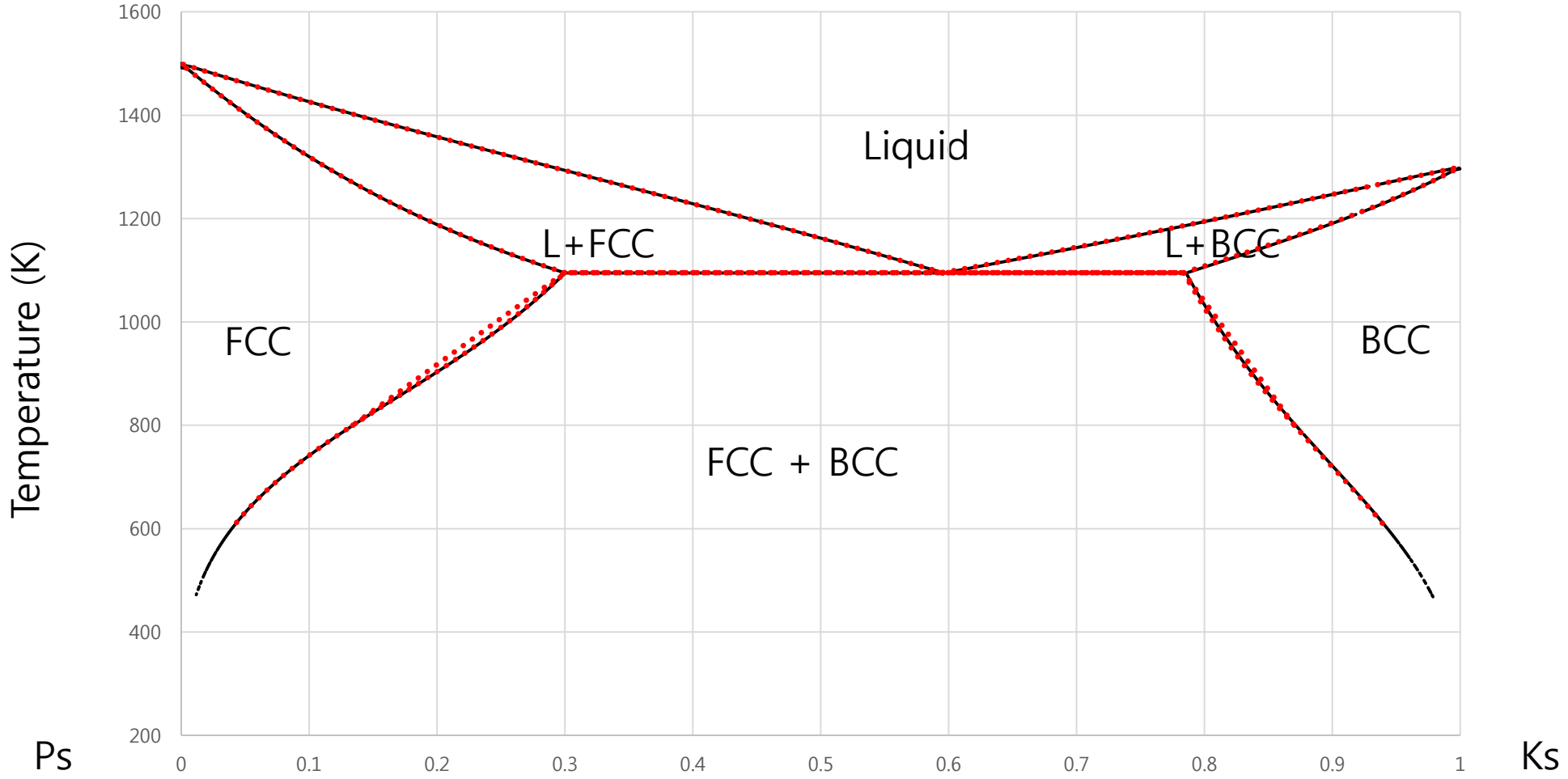
$$\mu_{Ps}^{L} - \mu_{Ps}^{BCC} = 0$$



	X_liquid	X_FCC	X_BCC	T
계산 값	0.596403	0.300249	0.785726	1094.67
실제 값	0.595539	0.299879	0.783978	1095.41
상대 오차	0.14508 %	0.12338 %	0.18470 %	0.06755 %

Midterm

Phase Diagram



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Code

```
double CP_Ks_liq(double X_Ks, double T) { ... }
double CP_Ps_liq(double X_Ks, double T) { ... }
double CP_Ks_fcc(double X_Ks, double T) { ... }
double CP_Ps_fcc(double X_Ks, double T) { ... }
double CP_Ks_bcc(double X_Ks, double T) { ... }
double CP_Ps_bcc(double X_Ks, double T) { ... }
double **jacobian_liq_fcc(double X_l, double X_f, double T) { ... }
double **jacobian_fcc_bcc(double X_f, double X_b, double T) { ... }
double **jacobian_liq_bcc(double X_l, double X_b, double T) { ... }
double *newton_method_liq_fcc(double Xl_ini, double Xf_ini, double T) { ... }
double *newton_method_fcc_bcc(double Xf_ini, double Xb_ini, double T) { ... }
double *newton_method_liq_bcc(double Xl_ini, double Xb_ini, double T) { ... }
double draw_liq_fcc(double X_ini, double _ini) { ... }
double **jacobian_triple(double X_l, double X_f, double X_b, double T) { ... }
double newton_method_triple(double Xl_ini, double Xf_ini, double Xb_ini, double T_ini) { ... }
```

Chemical Potential

Jacobian

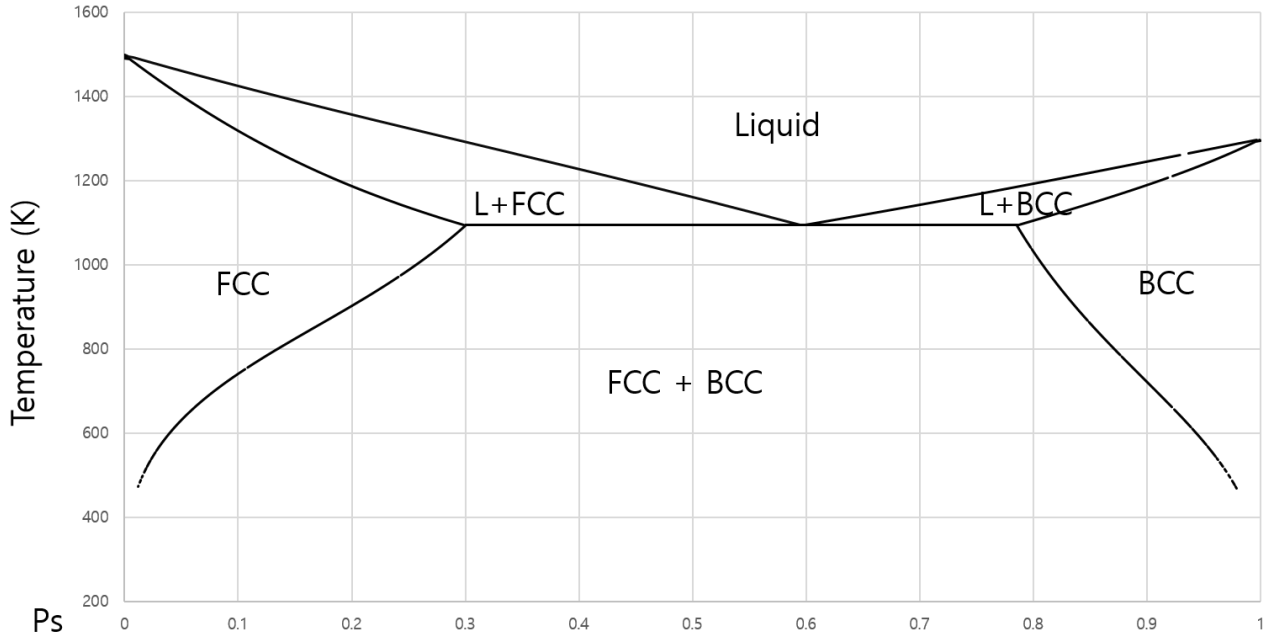
Newton Method

```
Jacob[0][0] = (R*T / X_l) - 2 * (L0_liq(T, 0) + 2 * L1_liq(T, 0) * X_l) * (1 - X_l) + 2 * L1_liq(T, 0)*pow((1 - X_
Jacob[0][1] = -(R*T / X_f) + 2 * (L0_fcc(T, 0) + 2 * L1_fcc(T, 0) * X_f) * (1 - X_f) - 2 * L1_fcc(T, 0)*pow((1 - X
Jacob[0][2] = 0;
Jacob[0][3] = -12.5 + R*(log(X_l) - log(X_f)) + ((L0_liq(T,1) + 2*L1_liq(T,1)*X_l)*pow((1-X_l),2)) - ((L0_fcc(T, 1
//////////////////////
Jacob[1][0] = (R*T / X_l) - 2 * (L0_liq(T, 0) + 2 * L1_liq(T, 0) * X_l) * (1 - X_l) + 2 * L1_liq(T, 0)*pow((1 - X_
Jacob[1][1] = 0;
Jacob[1][2] = -(R*T / X_b) + 2 * (L0_bcc(T, 0) + 2 * L1_bcc(T, 0) * X_b) * (1 - X_b) - 2 * L1_bcc(T, 0)*pow((1 - X
Jacob[1][3] = -12.5 + R*(log(X_l) - log(X_b)) + ((L0_liq(T, 1) + 2 * L1_liq(T, 1)*X_l)*pow((1 - X_l), 2));
//////////////////
Jacob[2][0] = -(R*T / (1 - X_l)) + 2 * (L0_liq(T, 0) + (2 * X_l - 1) * L1_liq(T, 0)) * (X_l)+2 * L1_liq(T, 0)*pow(
Jacob[2][1] = (R*T / (1 - X_f)) - 2 * (L0_fcc(T, 0) + (2 * X_f - 1) * L1_fcc(T, 0)) * (X_l)-2 * L1_fcc(T, 0)*pow((
Jacob[2][2] = 0;
Jacob[2][3] = -10 + R*(log(1-X_l) - log(1-X_f)) + ((L0_liq(T, 1) + (2*X_l -1) * L1_liq(T, 1))*pow((X_l), 2)) - ((L
//////////////////////
Jacob[3][0] = -(R*T / (1 - X_l)) + 2 * (L0_liq(T, 0) + (2 * X_l - 1) * L1_liq(T, 0)) * (X_l)+2 * L1_liq(T, 0)*pow(
Jacob[3][1] = 0;
Jacob[3][2] = (R*T / (1 - X_b)) - 2 * (L0_bcc(T, 0) + (2 * X_b - 1) * L1_bcc(T, 0)) * (X_b)-2 * L1_bcc(T, 0)*pow((
Jacob[3][3] = -10 + R*(log(1 - X_l) - log(1 - X_b)) + ((L0_liq(T, 1) + (2 * X_l - 1) * L1_liq(T, 1))*pow((X_l), 2)
```

```
Jacob[0][0] = (R*T / X_l) - 2 * (14894 - 7.99137*T + 2 * (-4794.92 - 0.0112334*T) * X_l) * (1 - X_l) + 2 * (-4794.92
Jacob[0][1] = -(R*T / X_f) + 2 * ((12597.6 - 4.99703*T) + 2 * (-7199.97 + 0.0224905*T) * X_f) * (1 - X_f) - 2 * (-719
Jacob[0][2] = 0;
Jacob[0][3] = -12.5 + R*(log(X_l) - log(X_f)) + (((-7.99137) + 2 * (- 0.0112334)*X_l)*pow((1 - X_l), 2)) - (((-4.9970
//////////////////////
Jacob[1][0] = (R*T / X_l) - 2 * (14894 - 7.99137*T + 2 * (-4794.92 - 0.0112334*T) * X_l) * (1 - X_l) + 2 * (-4794.92
Jacob[1][1] = 0;
Jacob[1][2] = -(R*T / X_b) + 2 * (6995.65 - 3.91579*T + 2 * 0 * X_b) * (1 - X_b) - 2 * 0*pow((1 - X_b), 2);
Jacob[1][3] = -12.5 + R*(log(X_l) - log(X_b)) + (((-7.99137) + 2 * (-0.0112334)*X_l)*pow((1 - X_l), 2));
//////////////////
Jacob[2][0] = -(R*T / (1 - X_l)) + 2 * (14894 - 7.99137*T + (2 * X_l - 1) * (-4794.92 - 0.0112334*T)) * (X_l)+2 * (-4
Jacob[2][1] = (R*T / (1 - X_f)) - 2 * ((12597.6 - 4.99703*T) + (2 * X_f - 1) * (-7199.97 + 0.0224905*T)) * (X_l)-2 *
Jacob[2][2] = 0;
Jacob[2][3] = -10 + R*(log(1 - X_l) - log(1 - X_f)) + (((-7.99137) + (2 * X_l - 1) * (-0.0112334))*pow((X_l), 2)) - (
//////////////////////
Jacob[3][0] = -(R*T / (1 - X_l)) + 2 * (14894 - 7.99137*T + (2 * X_l - 1) * (-4794.92 - 0.0112334*T)) * (X_l)+2 * (-4
Jacob[3][1] = 0;
Jacob[3][2] = (R*T / (1 - X_b)) - 2 * (6995.65 - 3.91579*T + (2 * X_b - 1) * 0) * (X_b)-2 *0*pow((X_b), 2);
Jacob[3][3] = -10 + R*(log(1 - X_l) - log(1 - X_b)) + (((-7.99137) + (2 * X_l - 1) * (-0.0112334))*pow((X_l), 2));
```

Midterm

Question & Answer



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반성할 점

- L 값을 계산한 뒤 대입하니 된다. 하지만 그래도 계산량이 많은지, Liquid – FCC와 Liquid – BCC를 한번에 못한다. (하나씩 주석 처리하며 계산했다.)
- Newton's Method에서 값이 나오지 않은 부분을 처리할 방법을 보충해야 한다. Cubic Spline도 나쁘지 않다고 생각.
- FCC와 FCC+BCC 사이의 선에서 오차가 발생했다.