109 學年度第二學期　材料熱力學二　期末考

$R = 8.314\ J\ K^{-1}\ mol^{-1} = 0.082\ L\ atm\ K^{-1} mol^{-1}$

1 A regular solution contains A and B, which obeys $\Omega = 18000\ J\ mol^{-1}$. Answer the following questions at 900 K.

1.1 **(5%)** Calculate the critical temperature.

1.2 **(5%)** Determine the spinodal compositions by the calculation, not from the curve.

1.3 **(10%)** Plot the curve of $\Delta G^M\ vs. X_B$.

1.4 **(10%)** Plot the curve of $a_B\ vs\ X_B$.

2 A and B are mutually dissolved in the liquid phase and the solid phase. Some thermal properties of A and B are given by:

	Melting Point (K)	$\Delta H_m^0\ (J\ mol^{-1})$
A	1100	11000
B	1700	13000

Set that the liquid phase and the solid phases are ideal and have the same heat capacities.

2.1 **(10%)** Plot $\Delta G_{(s)}^M\ vs. X_B$ and $\Delta G_{(l)}^M\ vs. X_B$ at 1400 K when $G_{A(l)}^0$ and $G_{B(s)}^0$ equal zero.

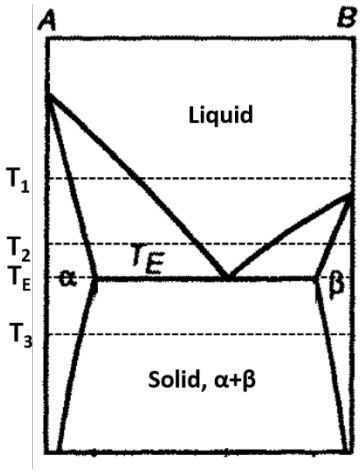
2.2 **(10%)** Plot $\Delta G_{(s)}^M\ vs. X_B$ and $\Delta G_{(l)}^M\ vs. X_B$ at 1400 K when $G_{A(l)}^0$ and $G_{B(l)}^0$ equal zero.

2.3 **(10%)** Plot the phase diagram with respect to X_B.

2.4 **(10%)** Plot the curve of $a_A\ vs. X_B$ with respect to pure solid A and the curve of $a_A\ vs. X_B$ with respect to pure liquid A at 1400 K. Please **label** the length of a_A at $X_A = 1$ for each curve.

2.5 **(10%)** Plot the curve of $a_B\ vs. X_B$ with respect to pure solid B and the curve of $a_A\ vs. X_B$ with respect to pure liquid B at 1400 K. Please **label** the length of a_B at $X_B = 1$ for each curve.

3 The phase diagram of the A-B binary system is shown on the right-hand side. If the liquid solution obeys the **positive deviation solution** and the solid solution is the **ideal solution,** please roughly plot the curves of $a_A\ vs. x_B$ and $a_B\ vs. X_B$ at various temperatures.



3.1 **(5%)** At T_1, set pure solid A and pure liquid B as the standard points.

3.2 **(5%)** At T_2, set pure solid A and pure solid B as the standard points.

3.3 **(5%)** At T_E (Eutectic T), set pure solid A and pure solid B as the standard points.

3.4 **(5%)** At T_3, set pure solid A and pure solid B as the standard points.

1.1 $\alpha = \frac{\Omega}{RT}$, $\alpha_{cr} = 2 = \frac{\Omega}{RT_{cr}}$

$T_{cr} = \frac{\Omega}{2R} = 1082.511K$ ※

1.2.

$\Delta G_m = RT(x_A \ln x_A + x_B \ln x_B) + \Omega x_A x_B$.

Spinodal Composition 为由稳态到不稳态，临界点在 $\frac{\partial^2 G^M}{\partial x_B^2} = 0$ 的地方，$\frac{\partial^2 \Delta G^M}{\partial x_B^2} < 0$ 为发生 Spinodal Composition

$\frac{\partial \Delta G_m}{\partial x_B} = RT(\ln x_B - \ln x_A) + \Omega(1-2x_B)$

$\frac{\partial^2 \Delta G_m}{\partial x_B^2} = RT\left(\frac{1}{x_A} + \frac{1}{x_B}\right) - 2\Omega$

当 $RT(\frac{1}{x_A} + \frac{1}{x_B}) < 2\Omega$

$\frac{1}{x_A} + \frac{1}{x_B} < \frac{2\Omega}{RT} = 4.8116 \Rightarrow \frac{1}{x_A} + \frac{1}{x_B} < 4.8116 \Rightarrow \frac{1}{1-x_B} + \frac{1}{x_B} < 4.8116$

$\Rightarrow 0.29464 < x_B < 0.70535$

∴ $0.29464 < x_B < 0.70535$ 会发生 Spinodal Composition

1.3.

$\Delta G^M = RT(x_B \ln x_B + (1-x_B)\ln(1-x_B)) + \Omega(x_B - x_B^2)$

图在后面

$x_A(1-x_B)$ $x_A(1-x_B)$

1.4

$\Delta \overline{G_B^M} = \Delta G^M + x_A \frac{d\Delta G^M}{dx_B} = RT \ln \alpha_B$.

$= RT(x_A \ln x_A + x_B \ln x_B) + \Omega x_A x_B + x_A\left(RT(\ln x_B - \ln x_A) + \Omega(1-2x_B)\right)$

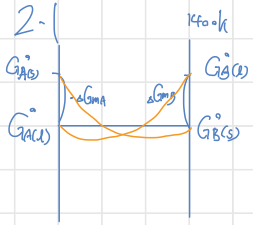
$= RT(x_A \ln x_A + x_B \ln x_B) + RT(x_A \ln x_B - x_A \ln x_A) + \Omega(x_A x_B + x_A - 2x_A x_B)$

$= RT \ln x_B + \Omega(x_A - x_A x_B) = RT \ln \alpha_B$

$\Rightarrow \ln \alpha_B = \ln x_B + \frac{\Omega}{RT}(x_A - x_A x_B) \Rightarrow \alpha_B = \exp\left(\ln x_B + \frac{\Omega}{RT} x_A^2\right)$

图在后面

2.1



$$\Delta G_{S\text{-}l} = -\frac{\Delta H_m}{T_m}(T - T_m)$$

$$\Delta G_{mA} = \Delta G^{A}_{S\text{-}l} = \frac{-11000}{1100}(1400 - 1100) = -3000$$

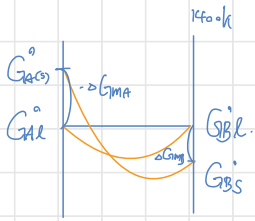
$$\Delta G_{mB} = \Delta G^{B}_{S\text{-}l} = \frac{-13000}{1700}(1400 - 1700) = 2294.117$$

图在反面

$$\Delta G^{M}_{l} = RT(x_A \ln x_A + x_B \ln x_B) + x_B \Delta G_{mB}$$

$$\Delta G^{M}_{S} = RT(x_A \ln x_A + x_B \ln x_B) - x_A \Delta G_{mA}$$

2.2



$$\Delta G^{M}_{l} = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta G^{M}_{S} = RT(x_A \ln x_A + x_B \ln x_B) - x_A \Delta G_{mA} - x_B \Delta G_{mB}.$$

2.3

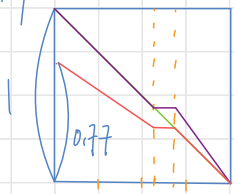
$$x_{B(l)} = 1 - x_{A(l)} = 1 - \frac{\left[1 - \exp\left(\frac{-\Delta G^{\circ}_{mB}}{RT}\right)\right]\exp\left(\frac{-\Delta G^{\circ}_{mA}}{RT}\right)}{\exp\left(\frac{-\Delta G^{\circ}_{mA}}{RT}\right) - \exp\left(\frac{-\Delta G^{\circ}_{mb}}{RT}\right)}$$

图在反面

$$x_{B(S)} = 1 - \frac{1 - \exp\left(\frac{-\Delta G^{\circ}_{mb}}{RT}\right)}{\exp\left(\frac{-\Delta G^{\circ}_{mA}}{RT}\right) - \exp\left(\frac{\Delta G_{mB}}{RT}\right)}$$

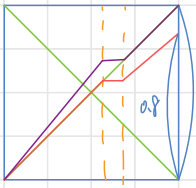
图在反面

2.4



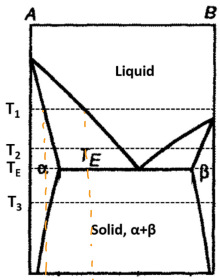
— liquid
— solid

2.5

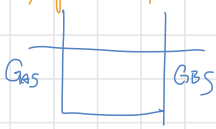


liquid
solid.

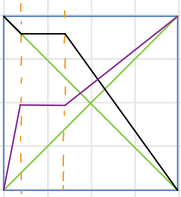
3.1



Solid ideal
Liqu. $\phi > 1$



a

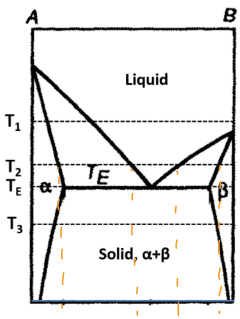


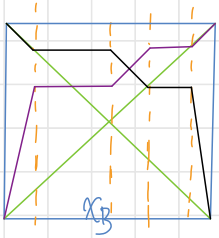
a_B

a_A

x_B

3.2



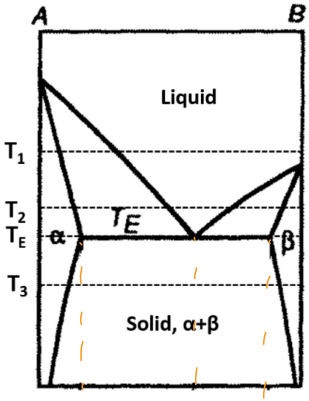


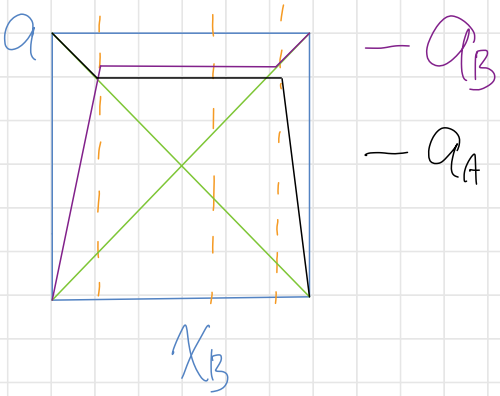
a_B

a_A

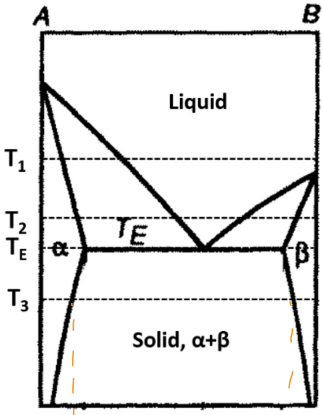
x_B

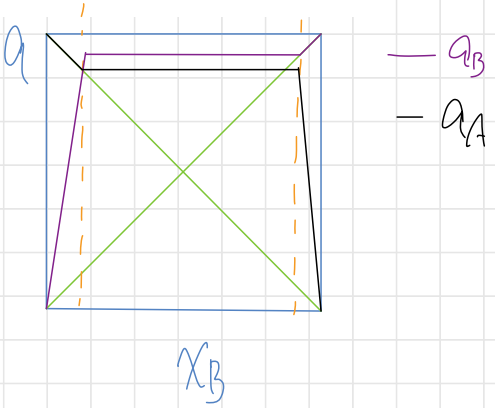
3.3



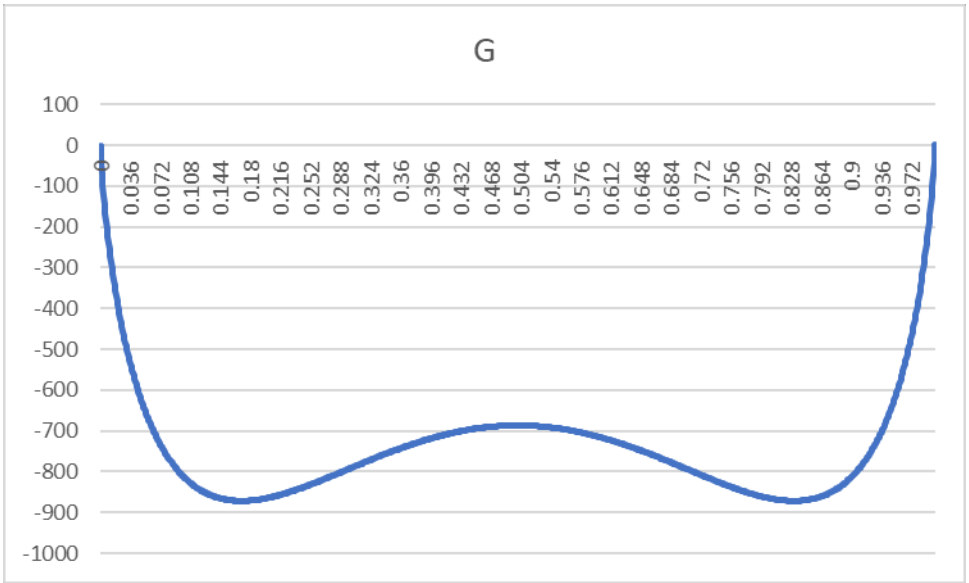


3.4

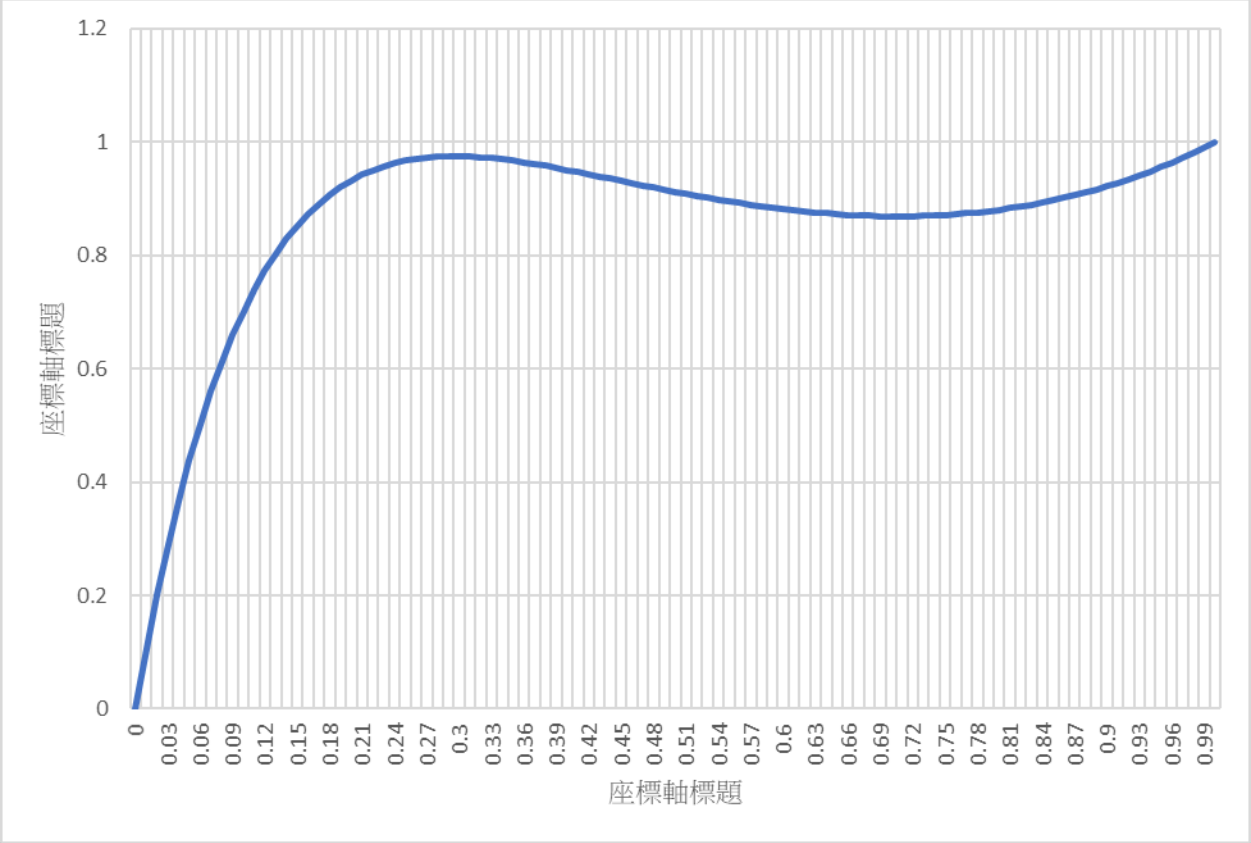




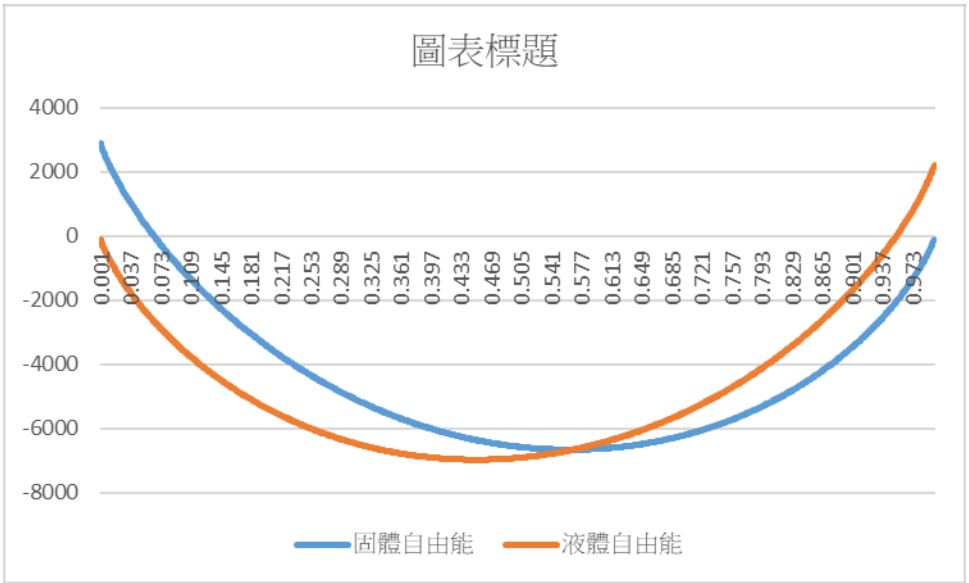
1.3


G
100
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
0
0.036
0.072
0.108
0.144
0.18
0.216
0.252
0.288
0.324
0.36
0.396
0.432
0.468
0.504
0.54
0.576
0.612
0.648
0.684
0.72
0.756
0.792
0.828
0.864
0.9
0.936
0.972

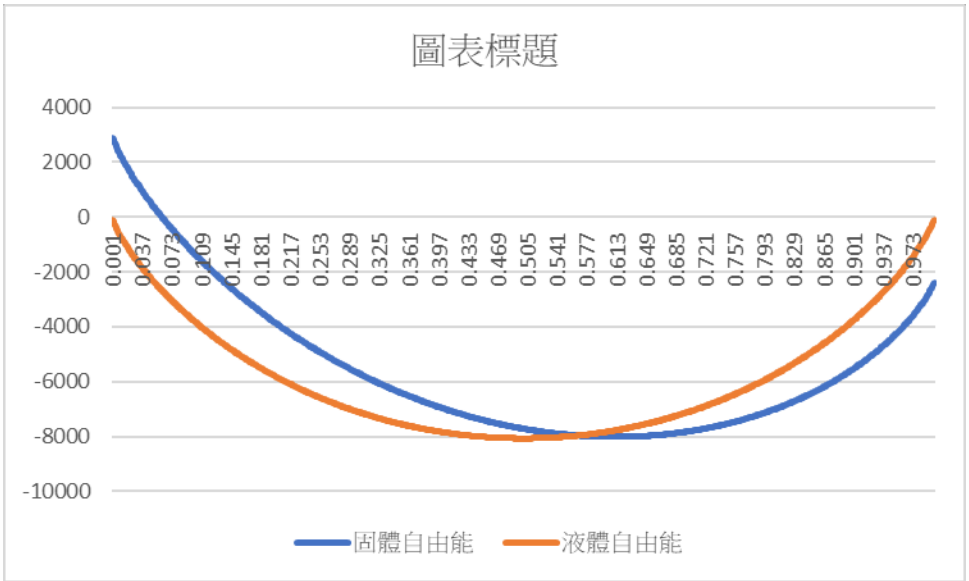
1.4


1.2
1
0.8
0.6
0.4
0.2
0
座標軸標題
0
0.03
0.06
0.09
0.12
0.15
0.18
0.21
0.24
0.27
0.3
0.33
0.36
0.39
0.42
0.45
0.48
0.51
0.54
0.57
0.6
0.63
0.66
0.69
0.72
0.75
0.78
0.81
0.84
0.87
0.9
0.93
0.96
0.99
座標軸標題

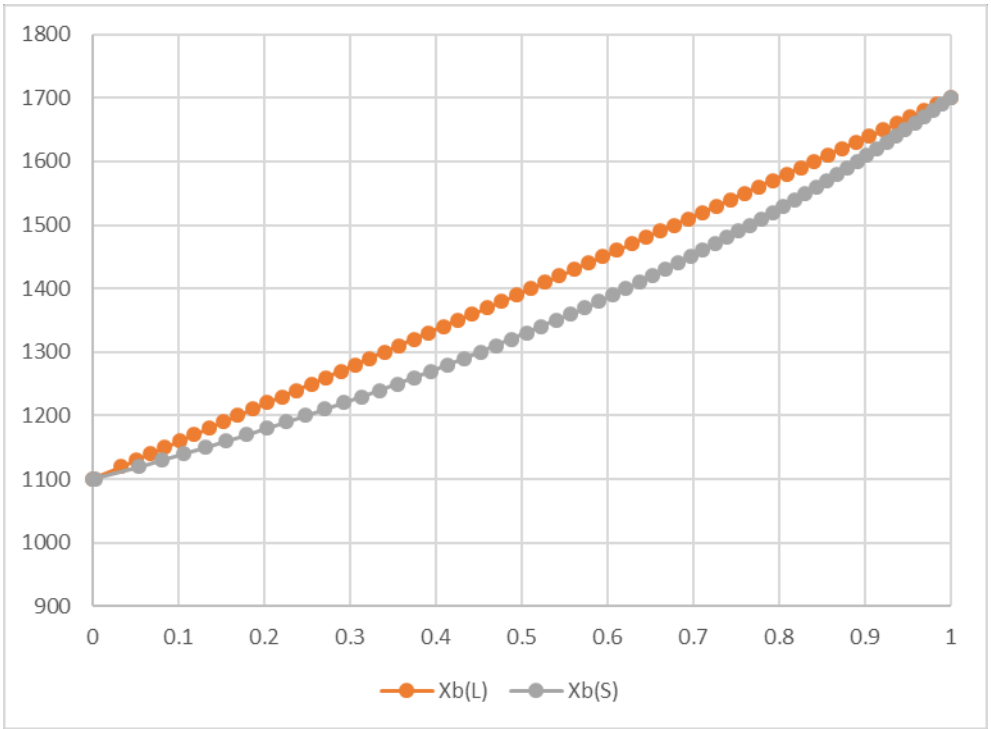
2.1


圖表標題
4000
2000
0
-2000
-4000
-6000
-8000
0.001
0.037
0.073
0.109
0.145
0.181
0.217
0.253
0.289
0.325
0.361
0.397
0.433
0.469
0.505
0.541
0.577
0.613
0.649
0.685
0.721
0.757
0.793
0.829
0.865
0.901
0.937
0.973
固體自由能
液體自由能

2.2


圖表標題
4000
2000
0
-2000
-4000
-6000
-8000
-10000
0.001
0.037
0.073
0.109
0.145
0.181
0.217
0.253
0.289
0.325
0.361
0.397
0.433
0.469
0.505
0.541
0.577
0.613
0.649
0.685
0.721
0.757
0.793
0.829
0.865
0.901
0.937
0.973
固體自由能
液體自由能

2.3


1800
1700
1600
1500
1400
1300
1200
1100
1000
900
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Xb(L)
Xb(S)