Diffusion in Multicomponent Solids
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Lecture 10 - Exercise: Solution Thermodynamics

Welcome to the course on Diffusion in Multicomponent Solids. Today is the 10th class in this course and I hope you guys are enjoying the class. Today, I am going to go over four exercise problems which I believe will help you guys to make clear some of the concepts. First three problems are from the assignment that you did last week and there will be one more problem that I will try to solve based on the Gibbs free energy composition diagrams.

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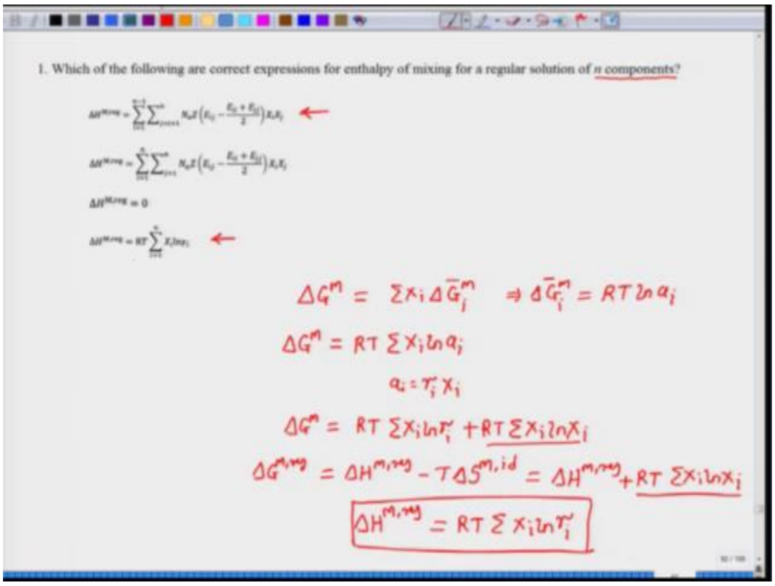

1. Which of the following are correct expressions for enthalpy of mixing for a regular solution of n components?

$\Delta H^{mixing} = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} N_a z\left(\varepsilon_{ij} - \frac{\varepsilon_{ii}+\varepsilon_{jj}}{2}\right) X_i X_j$ ←

$\Delta H^{mixing} = \sum_{i=1}^{n}\sum_{j=1}^{n} N_a z\left(\varepsilon_{ij} - \frac{\varepsilon_{ii}+\varepsilon_{jj}}{2}\right) X_i X_j$

$\Delta H^{mixing} = 0$

$\Delta H^{mixing} = RT\sum_{i=1}^{n} X_i \ln\gamma_i$ ←

$$\Delta G^m = \sum x_i \Delta\bar{G}_i^m \Rightarrow \Delta\bar{G}_i^m = RT\ln a_i$$

$$\Delta G^m = RT\sum X_i \ln a_i$$

$$a_i = \gamma_i X_i$$

$$\Delta G^m = RT\sum X_i \ln\gamma_i + \underline{RT\sum X_i \ln X_i}$$

$$\Delta G^{mixing} = \Delta H^{mixing} - T\Delta S^{m,id} = \Delta H^{mixing} + \underline{RT\sum X_i \ln X_i}$$

$$\boxed{\Delta H^{mixing} = RT\sum X_i \ln\gamma_i}$$

The first problem from the last assignment is:

Which of the following are correct expressions for enthalpy of mixing for a regular solution of n components?

we have derived the expression for enthalpy of mixing for a regular solution in a ternary system. This problem is about an n component system. If you remember the expression the enthalpy of mixing for a regular solution, it has the contribution from difference in the bond energies of dissimilar atom pairs and the average of the bond energies of the corresponding similar atom pairs.

If we compare the expressions, the first expression, i.e., option A seems to be the correct expression. Since, we need all the dissimilar type of atom pairs and there are n components, so i has to be varied from 1 to $n-1$ and $j \neq i$ for the dissimilar type of pairs. This varies from j equal to $i+1$ to n.

Based upon this expression if we deduce the expression for ternary, we will see that it will come out to be same expression as we derived in the class. For a ternary system i will be from 1 to 2 and j will be from 2 to 3. For i equal to 1 there will be E_{12}, and E_{13}, and for i equal to 2, there will be dissimilar pair of type E_{23}, of course the average of the bond energies of similar type of pairs. So, first one is the correct expression but there is one more expression which is also correct and that is the fourth one, option D.

Let us try to look into this. We know:

$$\Delta G^{m} = \sum X_i \Delta \bar{G}_i^{m}$$

where ΔG^{m} is the molar Gibbs free energy of mixing of the solution and $\Delta \bar{G}_i^{m}$ bar denotes the partial molar Gibbs free energy of mixing of i in the solution. X_i is the mole fraction of i and we know:

$$\Delta \bar{\bar{G}}_i^{m} = RT ln\, a_i$$

So,

$$\Delta G^{m} = RT \sum_{i=1}^{n} X_i ln\, a_i$$

But,

$$a_i = \gamma_i X_i$$

where γ_i is the thermodynamic activity coefficient. Therefore:

$$\Delta G^{m} = RT \sum_{i=1}^{n} X_i ln\, \gamma_i + RT \sum_{i=1}^{n} X_i ln\, X_i$$

Now, when we consider a regular solution, for regular solution:

$$\Delta G^{m,,reg} = \Delta H^{m,reg} - T\Delta S^{m,id}$$

Here, we assume that for a regular solution entropy of mixing is same as that for an ideal solution. So:

$$\Delta G^{m,\ reg} = \Delta H^{m,reg} - T\Delta S^{m,id} = \Delta H^{m,reg} + RT\sum_{i=1}^{n} X_i ln\, X_i$$

Now, if you compare this with the general expression for ΔG^m, these two terms will cancel out from both sides. So, we get:

$$\Delta H^{m,reg} = RT\sum_{i=1}^{n} X_i ln\, \gamma_i$$

This is the option D or the fourth expression here that should also be correct.

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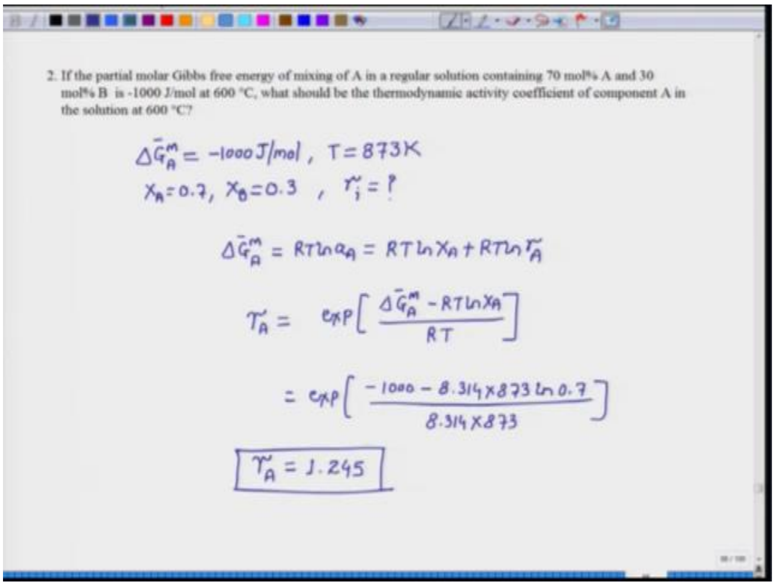

2. If the partial molar Gibbs free energy of mixing of A in a regular solution containing 70 mol% A and 30 mol% B is -1000 J/mol at 600 °C, what should be the thermodynamic activity coefficient of component A in the solution at 600 °C?

$$\Delta \bar{G}_A^m = -1000\, J/mol\ ,\ T = 873 K$$

$$X_A = 0.7,\ X_B = 0.3\ ,\ \gamma_i = ?$$

$$\Delta \bar{G}_A^m = RT ln\, a_A = RT ln\, X_A + RT ln\, \gamma_A$$

$$\gamma_A = exp\left[\frac{\Delta \bar{G}_A^m - RT ln\, X_A}{RT}\right]$$

$$= exp\left[\frac{-1000 - 8.314 \times 873\, ln\, 0.7}{8.314 \times 873}\right]$$

$$\boxed{\gamma_A = 1.245}$$

The second problem is, if the partial molar Gibbs free energy of mixing of A in a regular solution containing 70 mole percent of A and 30 mole percent of B is -1000 joule per mole at 600 °C, what should be the thermodynamic activity coefficient of component A in the solution at 600 °C? What is given here is partial molar Gibbs free energy of mixing of A:

$$\Delta \bar{G}_A^m = -1000 \frac{J}{mol} \quad , \qquad T = 873\, K$$

What should be the thermodynamic activity coefficient of component A?

The mole fractions are given as:

$$X_A = 0.7, \quad X_B = 0.3, \qquad \gamma_i = ?$$

We need to find out γ_i, the thermodynamic activity coefficient of i. Based on the last problem that we solved:

$$\Delta\bar{G}_A^m = RTln\, a_A = RTln\, X_A + RTln\, \gamma_A$$

If we rearrange the terms:

$$\gamma_A = \exp\left(\frac{\Delta\bar{G}_A^m - RTlnX_A}{RT}\right)$$

If we substitute the values of terms in the bracket we get:

$$\gamma_A = \exp\left(\frac{\Delta\bar{G}_A^m - RTlnX_A}{RT}\right) = \exp\left(\frac{-1000 - 8.314 \times 873 \times ln0.7}{8.314 \times 873}\right)$$

The answer comes out to be:

$$\gamma_A = 1.245$$

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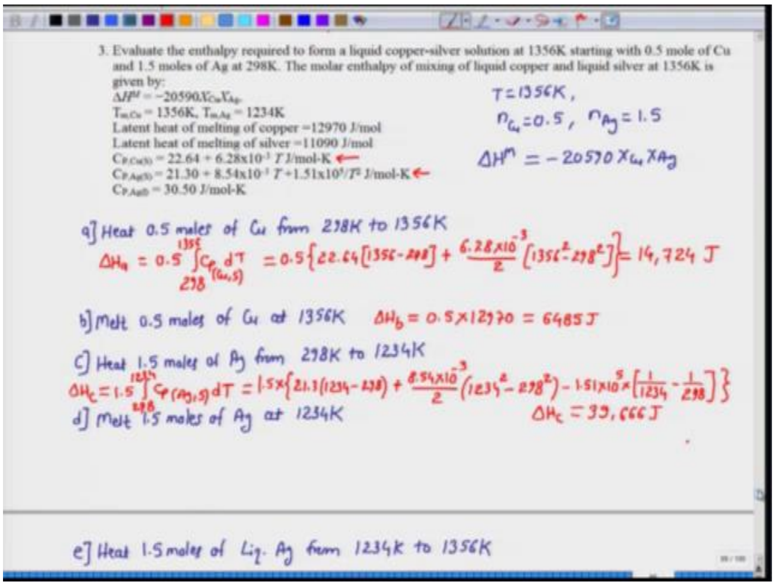


3. Evaluate the enthalpy required to form a liquid copper-silver solution at 1356K starting with 0.5 mole of Cu and 1.5 moles of Ag at 298K. The molar enthalpy of mixing of liquid copper and liquid silver at 1356K is given by:

$\Delta H^M = -20590 X_{Cu} X_{Ag}$

$T_{m,Cu} = 1356K$, $T_{m,Ag} = 1234K$

Latent heat of melting of copper = 12970 J/mol

Latent heat of melting of silver = 11090 J/mol

$C_{P,Cu(s)} = 22.64 + 6.28 \times 10^{-3}\, T$ J/mol-K ←

$C_{P,Ag(s)} = 21.30 + 8.54 \times 10^{-3}\, T + 1.51 \times 10^{5}/T^2$ J/mol-K ←

$C_{P,Ag(l)} = 30.50$ J/mol-K

$T = 1356K$,

$n_{Cu} = 0.5$, $n_{Ag} = 1.5$

$\Delta H^m = -20590 X_{Cu} X_{Ag}$

a] Heat 0.5 moles of Cu from 298K to 1356K

$$\Delta H_a = 0.5 \int_{298}^{1356} C_{p(Cu,s)}\, dT = 0.5\left\{22.64[1356-298] + \frac{6.28\times10^{-3}}{2}[1356^2-298^2]\right\} = 14,724\ J$$

b] Melt 0.5 moles of Cu at 1356K $\Delta H_b = 0.5 \times 12970 = 6485\,J$

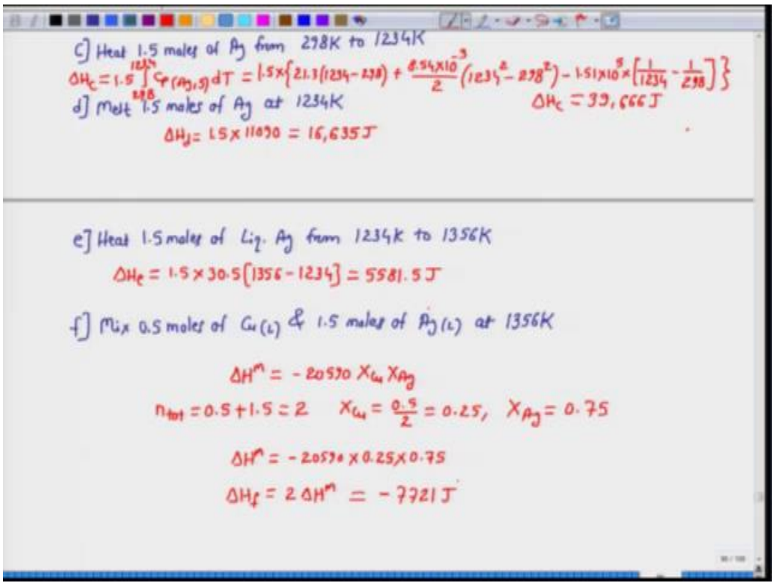
c] Heat 1.5 moles of Ag from 298K to 1234K

$$\Delta H_c = 1.5 \int_{298}^{1234} C_{p(Ag,s)}\, dT = 1.5 \times \left\{21.3(1234-298) + \frac{8.54\times10^{-3}}{2}(1234^2-298^2) - 1.51\times10^{5} \times \left[\frac{1}{1234} - \frac{1}{298}\right]\right\}$$

$\Delta H_c = 33,666\,J$

d] Melt 1.5 moles of Ag at 1234K

e] Heat 1.5 moles of Liq. Ag from 1234K to 1356K



c] Heat 1.5 moles of Ag from 298K to 1234K

$\Delta H_c = 1.5 \int_{298}^{1234} C_p(Ag,s)\,dT = 1.5\times\left\{21.3(1234-298) + \frac{8.54\times10^{-3}}{2}(1234^2-298^2) - 1.51\times10^{5}\times\left[\frac{1}{1234}-\frac{1}{298}\right]\right\}$

$\Delta H_c = 33{,}666\,J$

d] Melt 1.5 moles of Ag at 1234K

$\Delta H_d = 1.5\times 11090 = 16{,}635\,J$

e] Heat 1.5 moles of Liq. Ag from 1234K to 1356K

$\Delta H_e = 1.5\times 30.5[1356-1234] = 5581.5\,J$

f] Mix 0.5 moles of $Cu(l)$ & 1.5 moles of $Ag(l)$ at 1356K

$\Delta H^m = -20590\,X_{Cu}X_{Ag}$

$n_{tot} = 0.5+1.5 = 2 \quad X_{Cu} = \frac{0.5}{2} = 0.25, \quad X_{Ag} = 0.75$

$\Delta H^m = -20590\times0.25\times0.75$

$\Delta H_f = 2\,\Delta H^m = -7721\,J$

The next problem deals with evaluating the enthalpy of mixing at some higher temperature starting from the constituent elements at room temperature. The problem states, evaluate the enthalpy required to form a liquid copper-silver solution at 1356 Kelvin. T here is given as 1356 Kelvin starting with 0.5 moles of copper and 1.5 moles of silver, and initially they were at 298 Kelvin. The molar enthalpy of mixing of liquid copper and liquid silver. ΔH^m for this liquid solution at 1356 Kelvin can be given as:

$$\Delta H^m = -20590 \times (X_{Cu}X_{Ag})$$

And the latent heats of melting of both copper and silver are given as well as the heat capacities of solid copper, solid silver and liquid silver. Now, when we form this solution at 1356 Kelvin, it is to be remembered that the melting point of silver is 1234 Kelvin and melting point of copper is given is 1356 Kelvin. The melting point of silver is lower than the temperature. As we heat silver from 298 Kelvin it will undergo melting at 1234 Kelvin and then from 1234 to 1356 Kelvin we need to heat the liquid silver.

Copper, we will heat from 298 Kelvin to 1356 Kelvin and then we will melt copper at 1356 Kelvin which is the equilibrium melting point of copper and then we mix the two liquids to form a liquid solution. There are the steps involved:

(a) First we need to heat 0.5 moles of copper from 298 Kelvin to 1356 Kelvin
(b) Melt 0.5 moles of copper at 1356 Kelvin.
(c) Heat silver and 1.5 moles of silver from 298 to its melting point 1234 Kelvin
(d) Melt 1.5 moles of silver at 1234 Kelvin.
(e) Heat 1.5 moles of liquid silver from 1234 Kelvin to 1356 Kelvin

(f) Now, once we have both silver and copper in liquid form at 1356 Kelvin, we will mix them to form a solution.

We need to evaluate the enthalpy change for each of this process from $a \rightarrow f$ and we need to add them to get the total enthalpy required.

(a) If we consider the step a heat required for heating 0.5 moles of solid copper from 298 Kelvin to 1356 Kelvin should be:

$$\Delta H_a = 0.5 \int_{298}^{1356} C_{P\ (Cu.\ s)} dT$$

$C_{P\ (Cu.\ s)}$ is basically CP of solid copper.

If you look into the expression for C_P of solid copper here, we can write:

$$\begin{aligned} \Delta H_a &= 0.5 \int_{298}^{1356} C_{P\ (Cu.\ s)} dT \\ &= 0.5 \left\{ 22.64 \times (1356 - 298) + \frac{6.28 \times 10^{-3}}{2} \times (1356^2 - 298^2) \right\} \\ &= 14724\, J \end{aligned}$$

If we evaluate this, this comes out to be 14,724 Joules.

Remember we are considering 0.5 moles of copper we need to multiply integral $C_{P\ (Cu.\ s)} dT$ by number of moles which is 0.5.

(b) Then, for melting 0.5 moles of copper the enthalpy required is :

$$\Delta H_b = 0.5 \times 12970 = 6485\, J$$

ΔH_b is 0.5 times latent heat of melting of copper, which is given here as 12970.

(c) The process c is heating 1.5 moles of silver, solid silver from 298 Kelvin to 1234 Kelvin:

$$\Delta H_c = 1.5 \int_{298}^{1234} C_{P\ (Ag.\ s)} dT$$

This C_P is of solid silver:

$$\Delta H_c = 1.5 \int_{298}^{1234} C_{P\,(Ag.\ s)} dT$$

$$= 1.5 \left\{ 21.3 \times (1234 - 298) + \frac{8.54 \times 10^{-3}}{2} \times (1234^2 - 298^2) - 1.51 \times 10^5 \times \left(\frac{1}{1234} - \frac{1}{298} \right) \right\} = 39666\, J$$

(d) Then process d is melting of silver, 1.5 moles of silver. ΔH_d would be 1.5 times latent heat of silver given as 11090:

$$\Delta H_d = 1.5 \times 11090 = 16635\, J$$

(e) Once the silver is melted, process e is heating 1.5 moles of liquid silver from 1234 to 1356 and:

$$\Delta H_e = 1.5 \int_{1234}^{1356} C_{P\,(Ag.\ l)} dT$$

$C_{P\,(Ag.\ l)}$ given here is a constant. So:

$$\Delta H_e = 1.5 \times 30.5 \times (1356 - 1234) = 5581.5\ J$$

(f) And process f is mixing 0.5 moles of copper and 1.5 moles of silver both in liquid form to form the final liquid solution. The enthalpy of mixing for forming this solution is given as:

$$\Delta H^m = -20590 \times (X_{Cu} X_{Ag})$$

Remember this is the molar enthalpy of mixing. We are considering the total number of moles to be:

$$n_{Total} = 0.5 + 1.5 = 2$$

$$X_{Cu} = \frac{0.5}{2} = 0.25$$

$$X_{Ag} = 0.75$$

The molar enthalpy of mixing at 1356 Kelvin would come out to be:

$$\Delta H^m = -20590 \times 0.25 \times 0.75$$

$$\Delta H_f = 2\Delta H^m = -7721\, J$$

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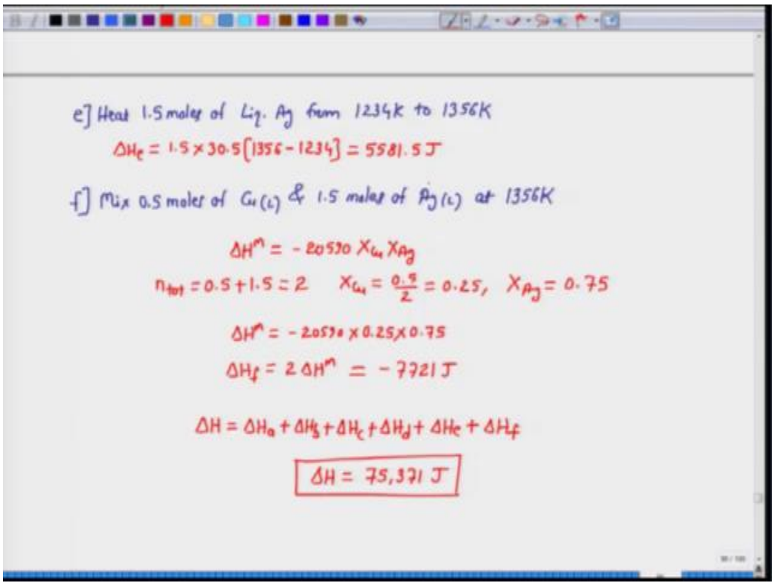

e] Heat 1.5 moles of Liq. Ag from 1234K to 1356K

$\Delta H_e = 1.5 \times 30.5 [1356 - 1234] = 5581.5\,J$

f] Mix 0.5 moles of Cu(l) & 1.5 moles of Ag(l) at 1356K

$\Delta H^m = -20590\, X_{Cu} X_{Ag}$

$n_{tot} = 0.5 + 1.5 = 2 \quad X_{Cu} = \frac{0.5}{2} = 0.25, \quad X_{Ag} = 0.75$

$\Delta H^m = -20590 \times 0.25 \times 0.75$

$\Delta H_f = 2\,\Delta H^m = -7721\,J$

$\Delta H = \Delta H_a + \Delta H_b + \Delta H_c + \Delta H_d + \Delta H_e + \Delta H_f$

$\boxed{\Delta H = 75{,}371\,J}$

The total enthalpy change or the total heat required to form the solution at 1356 Kelvin starting from copper at 298 Kelvin and silver at 298 Kelvin would be the summation of heat exchange from a to f:

$$\Delta H = \Delta H_a + \Delta H_b + \Delta H_c + \Delta H_d + \Delta H_e + \Delta H_f = 75371$$

This is how we can evaluate the enthalpy of mixing to form a solution from its pure constituents.

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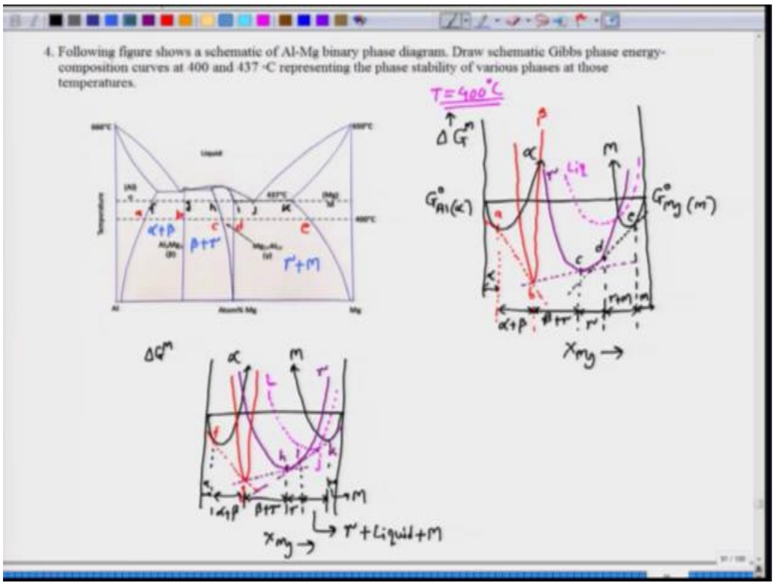

4. Following figure shows a schematic of Al-Mg binary phase diagram. Draw schematic Gibbs phase energy-composition curves at 400 and 437 °C representing the phase stability of various phases at those temperatures.

Now let us look into fourth problem, the first three problems were from the assignment last week. Now, I want to go over this because this will make some of the concepts clear of how do we use the Gibbs free energy composition diagrams to get to the phase diagrams.

Typically in computational thermodynamics we will need the Gibbs free energy data. We will draw the Gibbs free energy composition diagrams for the solutions and from there we will decide the phase stability and draw the phase diagrams. But, for simplicity of understanding let us go in a reverse way i.e., the phase diagram is given and we would like to draw schematically the Gibbs free energy versus composition diagrams which would represent the given phase stabilities.

So, this is an aluminum magnesium phase diagram. I would like to note here that this is a schematic diagram and not an accurate phase diagram. This is not complete because there is a r phase which appears between the β and γ phases which is missing and also the β phase has some solid solubility on both sides but I have shown it as a line compound for this exercise.

So we have to draw the schematic Gibbs free energy composition curves at 400 and 437 ℃. First look into 400 ℃ line. Let us mark this points as $a, b, c, d, and\ e$. We can see that up to a there is a single phase α solution that is stable. This is basically the FCC solution of magnesium and aluminum and b corresponds to the line compound β which is an intermetallic $\mathrm{Al_3Mg_2}$. Between a and b there should be a two phase region $\alpha + \beta$.

Similarly, between c and d there is a single phase stability of γ which is another intermetallic with the stoichiometry $\mathrm{Mg_{17}Al_{12}}$ and between $b\ and\ c$ there is a two phase stability region $\beta + \gamma$ and beyond e again the single phase solid solution is stable. This is basically the HCP solid solution of aluminum and magnesium. Between $d\ and\ e$ there is a two phase stability region of $\gamma + M$, M is the magnesium solid solution.

Now, when we draw the Gibbs free energy composition diagram, we will first fix the reference points or what we call as standard states and the reference points for G we take as the stable state of pure element at the given temperature. So at 400 ℃ both pure aluminum and pure magnesium are stable as solid phases more specifically aluminum as FCC solid and magnesium as HCP solid. So zeros will be at $G^{o}_{Al\ (\alpha)}$, this phase is called α FCC and the reference point for magnesium would be $G^{o}_{Mg\ (M)}$ or HCP and we have four phases at 400 ℃, $\alpha, \beta, \gamma\ and\ M$ and there is a fifth phase which is not stable at this temperature but we can see in the phase diagram.

So, we need at least 5 Gibbs free energy curves one for each of the phases. We will draw two curves for the terminal solutions α and M. This is Gibbs free energy curve for α and let us say this is for M phase. Now, there is a two phase region between α and β when we draw the

Gibbs free energy curve for β which is a line compound, we expect the curve to be very sharp. We should be able to draw a common tangent between the curve for α and β. And that common tangent should give the two phase configuration which has the lowest Gibbs free energy between points $a\ and\ b$ which are the touching points of the common tangents of the two curves.

Since the curve for β is very sharp whichever tangent we draw it should almost touch at the same point. This is point b. Then there is also a two phase region between β and γ as well as a two phase region between γ and M. We should draw the curve for γ such that there should be a common tangent between β and γ and another common tangent between γ and M and there is some solid solubility range from $c\ to\ d$ for γ. The curve for γ should not be as sharp as that for β. So, we draw one tangent between β and γ which will give contact points $b\ and\ c$ and another common tangent between γ and M which will give contact point $d\ and\ e$.

Now when we draw this curve, we have to take care that the curve for γ should not lie entirely above the common tangent between β and M. Otherwise what would happen? Stability will change because then two phase equilibrium will be between β and M and the γ field will not be stable at all. Because, then any composition between the two touching points will split into two phases β and$M$, then that will give the lowest Gibbs free energy configuration. So, as we can see up to point a, α phase has a lowest Gibbs free energy and this is the α stability region. Between $a\ and\ b$, α+β are stable. Because β it is a line compound it is stable only at composition b. Between $b\ and\ c$ again the two phase stability region β+γ exists, between c and d, γ single phase stability exists, beyond e single phase M is stable and between $d\ and\ e$ there is a two phase stability γ + M.

Now, liquid is not stable at any composition, the liquid will lie above all these tangents. So, this was at 400 °C and we are drawing ΔG^m versus X_{Mg}. Now how the situation will change at 437 °C? We see a specific feature at 437 °C, there exists a eutectic or the three phase stability region at 437 °C. Now if we label these points as f, g, h, i, j, k between points $i\ and\ k$, there is a three phase stability region, $\gamma + liq + M$.

That means I should be able draw a common tangent to all the three curves. The curve between γ, $M$and liquid. The liquid curve has come relatively downwards such that now the tangent to $M$and γ is also touching the liquid curve.

The others will not change much except that the solubility range for γ has now increased a little bit. So, if we draw ΔG^{m} versus X_{Mg} this is for α and this is for M. β is line compound, so its curve will be sharp and we can draw a common tangent. This gives me point $f\ and\ g$ as common tangent points. Then, curve between γ and β will give common tangent points $g\ and\ h$. Common tangent for M and γ will give points $i\ and\ k$. The liquid curve would lie such that the common tangent between γ and M should also touch the liquid curve which will give touching point j.

So, if you look at the phase stability again, up to point f, α is stable, $f\ to\ g$, α+ β two phase equilibrium. Exactly at point g β is stable, between $g\ and\ h$ two phase stability region β+γ, between $h\ and\ i$ single phase γ exists and between $i\ and\ k$, there is a three phase stability region, the phase stability is $\gamma + liq + M$ and beyond k single phase M exists.

This is how we should be able to draw the Gibbs free energy composition diagram from phase diagrams. We will stop here for today. Thank You.