Thermodynamics: Classical to Statistical

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Lecture 13

Phase diagram of three component system; one dimensional random walk

So far we have discussed the phase diagram of one component systems and two component systems. Today we will discuss the phase diagram of three component systems. First what we need to do, we need to draw one equilateral triangle, then we have to divide its side of the triangle into 10 equal parts and then we have to join the opposite points (Figure 1).

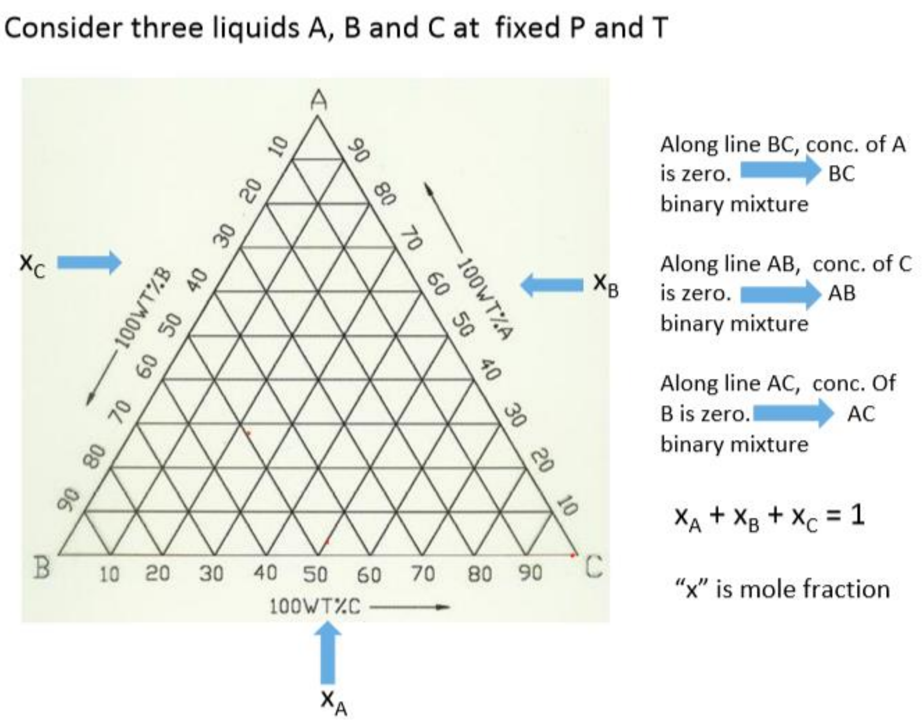


Figure 1

Like here first we need to draw one equilateral triangle like ABC. We have suppose three liquids, liquid A, liquid B and liquid C and at a given pressure and temperature, we are going to draw the phase diagram of the three component systems containing A, B, and C. first we will draw one equilateral triangle and then we have divided each side into 10 equal parts and then we join the opposite sides. Now along line BC, if you consider the line BC here, this B and this C, along this line, the concentration of A is zero, so concentration of A increases you can see the arrow here. Here, x_A, x_B and x_C are the mole fractions of A, B and C and sum of their mole fraction equals to 1. So the concentration of A increases from like this and then concentration of B increases from here, from like this, and concentration of C increases along this line. Along this line BC, concentration of A is zero along, similarly the concentration of B along line AC is zero and concentration of C along AB line is zero. So along line BC, since the concentration of A is zero, we get a binary mixtures containing B and C, similarly, since along the line AC the concentration of B is zero, we get binary mixtures of component A and B and along line AB since the concentration of C is zero, we get binary mixtures of A and C.

Now we know how to draw one equilateral triangle for a three component systems (Figure 2). Now, let us consider three different points here, three different composition mixture rather. Here for point a, mole fraction of A is 0.2, mole fraction of B is 0.8 and mole fraction of C is zero. If you go back and check, the mole fraction of C is zero along AB line. So the point will fall along AB line. Now x_A is 0.2 and x_B is 0.8. So we have to 20 percent A and 80 percent B. If you go back and check, x_A increases from like this. x_A is 0.2 and x_B is 0.8 means it will fall here. So this point A is corresponds to mole fraction of A is 0.2 and mole fraction of B is 0.8 and mole fraction of C is 0.

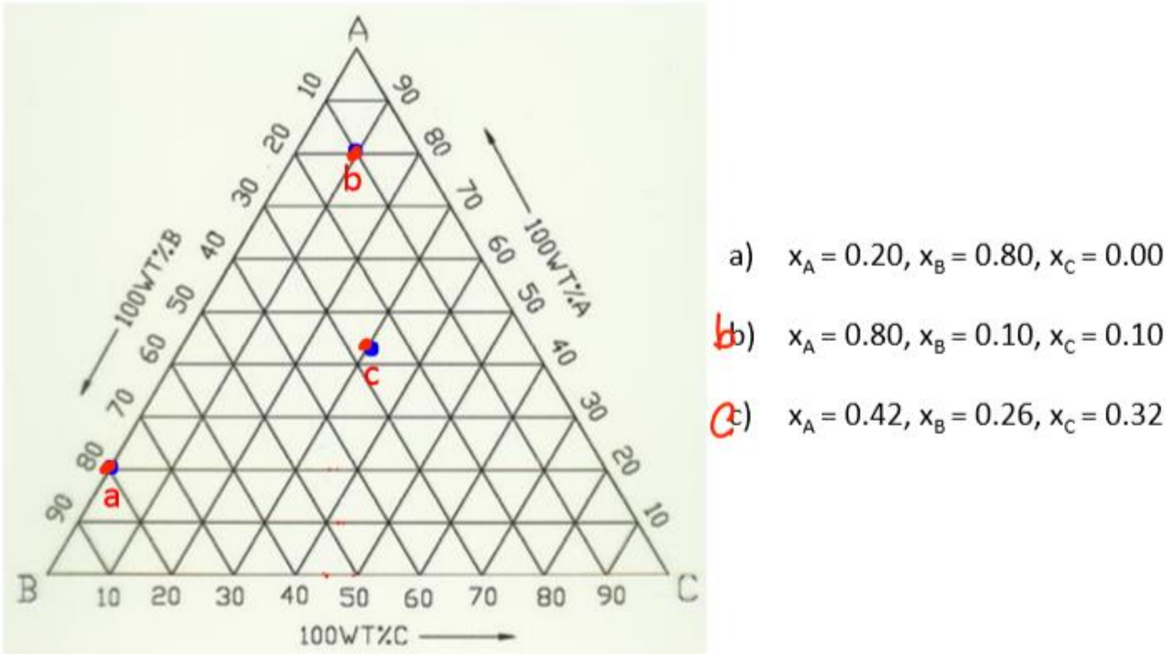


Figure 2

Now we have considered two more composition mixtures. The second composition mixture we considered is x_A is 0.8, x_B is 0.1 and x_C is 0.1. We have to go, this is along here or here. Along this line as I said x_A is zero, so here X_A is 1, 2, 0.1, 0.2, 0.3 like this it goes like this. x_A is 0.8, x_B is 0.1 and x_C is 0.1. It will fall here. Now we consider another composition mixture where the concentration of A is 0.42 or the mole fraction of A is 0.42, mole fraction of B is 0.26 and mole fraction of C is 0.32. So it will fall very near to this approximately here, very near to this point. So in this way if one gives you any composition mixture you for a three component system you can really locate the point.

Now we will consider one real ternary system or three component system. We consider water, acetic acid and chloroform ternary mixture at room temperature and 1 bar pressure (Figure 3). This is the phase diagram for water, acetic acid and chloroform ternary mixture.

Water-Acetic Acid-Chloroform Ternary Mixture at 298 K Temperature and 1 bar Pressure

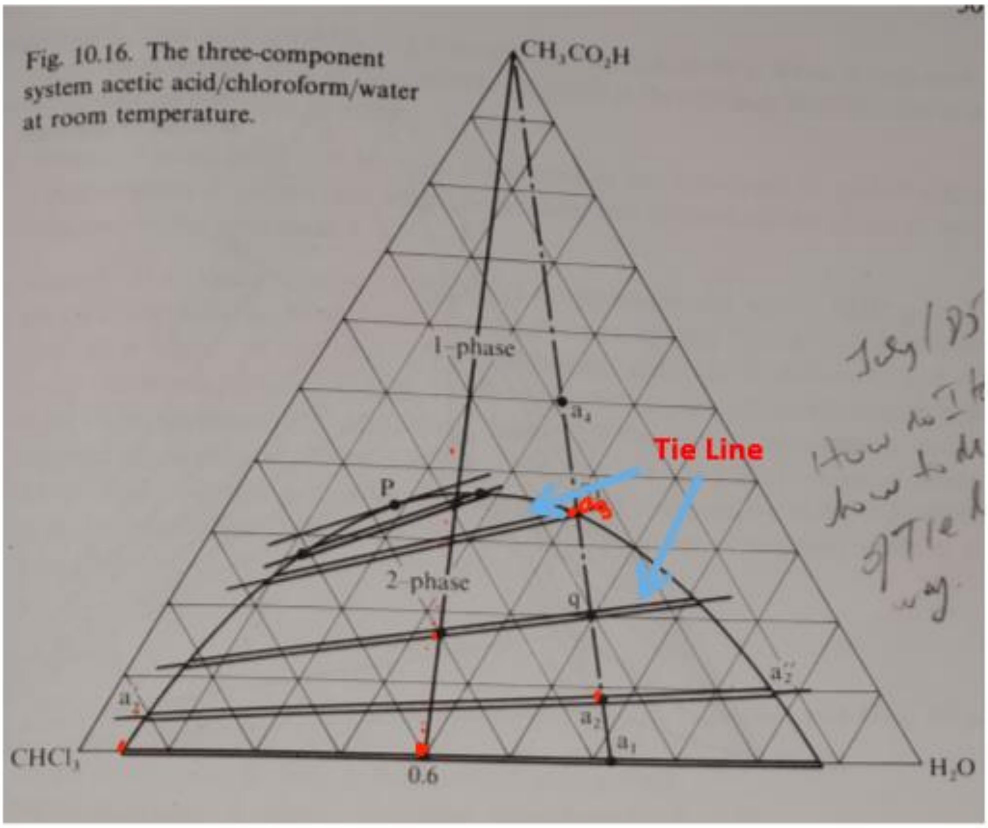


Figure 3

What are the salient features here?

i) Water and acetic acid are completely miscible in all proportions.

ii) Second point is chloroform and acetic acid are completely miscible in all proportions. So water and acetic acid they are completely miscible in all proportions, chloroform and acetic acid are completely miscible in all proportions.

iii) Point number 3 is, but water and chloroform are partially miscible they are not completely miscible.

iv) One phase system will be formed from a two phase water - chloroform mixture if acetic acid is added at highest. At high acetic acid concentration they will form one phase system irrespective of initial proportions of chloroform and water.

What is said here? Suppose we are starting from somewhere this point. At this point the concentration of acetic acid is zero. Now what we do, we keep on adding acetic acid along this line, we have two phase, two phase and two phase, and here we get one phase system. So if we have high acetic acid concentration, we get one phase system. Now few more thing here is, water and chloroform they are completely miscible in these regions, so two phase system is formed within these boundary.

We will discuss few more things about this curve.

i) If we follow the line a_1, a_2, a_3 and a_4, we observe that at some point a_2 the solution still has two phases but there is more water in chloroform phase, the phase at a_2` and more chloroform in water phase, the phase at a_2``. You go back and check it. If we have this composition at $a_2$, so we get two phases, one is at $a_2$` another is $a_2$``.

ii) There is more acetic acid in water rich phase than in chloroform rich phase because as a_2`` is near the acetic acid apex than a_2`.

iii) At point a_3 two phases are still present but the chloroform rich layer is there only trace amount, so at point a_3 still two phases are there but what the amount of chloroform is very very small.

iv) The point a_3 is called isothermal critical point or the plait point.

v) If we add acetic acid further to go to point a_4, the whole system is single phase. So point a_3 is called isothermal critical point or the plait point.

vi) The tie line, the line connecting a_2` and a_2`` represents that the solubility of acetic acid, water and chloroform, these line can be slanted or parallel. So these are the tie lines represented in blue arrow, they represent the solubility of acetic acid in two different medium, one in chloroform and other in water. Since the solubilities are different, solubility of chloroform, solubility of acetic acid is different in water than that of in chloroform, so here we get the slanted lines. These are experimental line. That is all about phase diagram of three component system.

One Dimensional Random Walk

Next we move to one dimensional random walk. Why it is important? The random walk is central to statistical physics and it is essential in predicting how fast one gas will diffuse into other and how fast heat will spread in a solid. These things are important, so it is important to know one dimensional random walk. How do we basically start with? We consider simple or simplest way to understand one dimensional random walk is, flip a coin and take a step:

i) Walk along a line, each space being the same length.

ii) Before each step, flip a coin.

iii) If it is heads, take one step forward and if it tails take one step back.

iv) The coin is "unbiased". So, the chances of heads and tails are equal.

So the probability of having heads is half, because a coin can have either heads or tails and a coin is unbiased means there is no biasness about your head, outcome of head and tails are equal. So this is how one can carry out the one dimensional random walk. What is the problem here? The problem here is to find the probability of landing at a given spot say n after a given number of steps N. So you keep on flipping a coin and you are flipping the coin N times and in between you get some heads, some tails and combination of this and then at the end suppose you are here, this is your end point. So what is the probability to land here which is end step? Suppose end step the distance between the starting point and end point is small n step. But you are taking capital N number of steps means you are flipping the coin capital N number of times, so that is the problem here. Now, how we can work out? We define a quantity first here. So the quantity we are defining here is $f_N(n)$ which is the probability of finding the particle beginning at zero, ending at n after N steps. So, we will go very very slowly here. Suppose for a walk of zero step, zero step means we have not done anything yet, so in that case what is the probability $f_0(0)$, this is 1.

$$f_0(0) = 1$$

Now, for a walk of one step, here capital N is 1 and what is small n here? when capital N is 1 so either you go in the positive direction (one step in the forward direction) or in the negative doirection (one step backward). So we get n equals to +1 or n equals to –1. so what is the probability of having +1? You are flipping the coin, how many times you are flipping the coin here? Only one time and you are going either one step forward or one step backward, so for in both cases the probability is half. So, $f_1(+1)$ is 1/2 and $f_1(-1)$ is also 1/2.

$$f_1(+1) = 1/2 \text{ and } f_1(-1) = 1/2$$

Next we consider for walk of two steps. Two steps means capital N equals to 2, basically you are flipping the coin twice, so what could be the outcome?

HH(+2)　　HT(0)　　TH(0)　　TT(–2)

So in both cases you can get heads, so we write H and H, you get first heads and then get tails, the third possibility is you get first tails and then you get heads and the last outcome is you can get both tails right.If you get head and heads in both the times, for one heads you are going one step in the forward direction, for two heads you get two step in the forward direction. Now for HT case, first heads means you get one step forward, then tail means one step backward, so you get +1 and –1 so basically it gives you 0. So there is no change from your starting point. Similarly for TH also you get 0. When both, in both cases you get tails, so you get, you are going 2 step backward, so you get minus. So what is the probability there? For HH,

$$f_2(+2) = 1/4$$

Means you are getting HH one time and total number is 4. so you get 1 by 4 probability. Then for HT and TH,

$$f_2(0) = 1/2$$

For TT we get,

$$f_2(-2) = 1/4$$

Next we consider three steps, so for a walk of three steps, N equals to 3 because total number of steps we are taking here is 3. What are the outcomes?

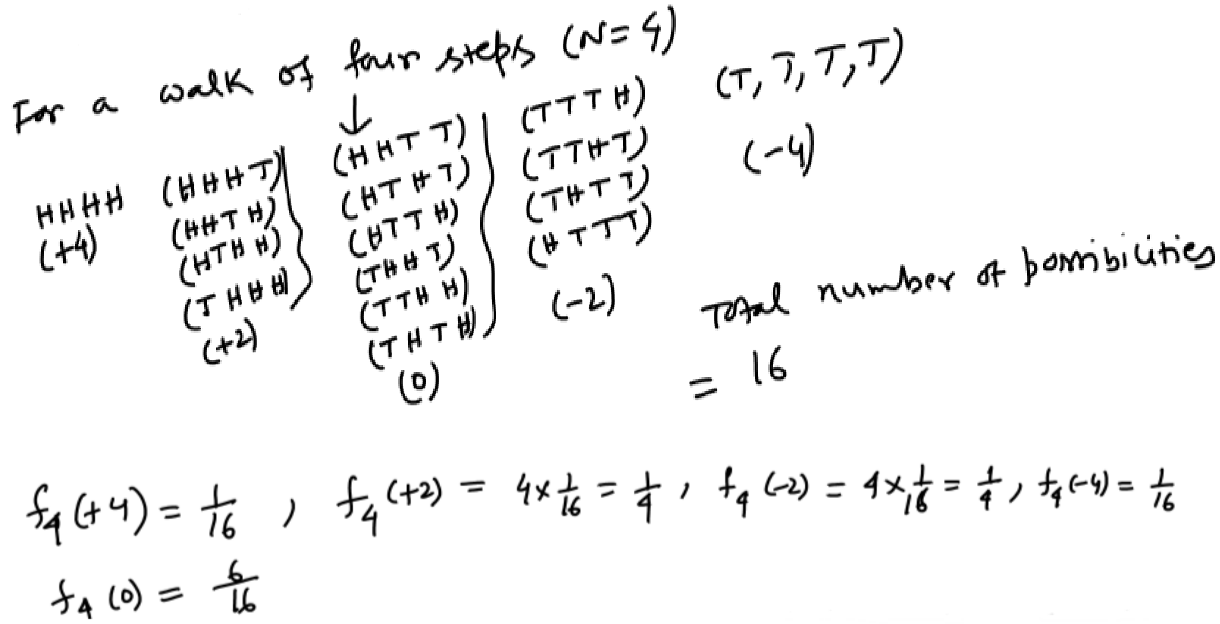
For a walk of three steps $(N=3)$

HHH $(+3)$, (HHT) $(+1)$, (HTH) $(+1)$, (THH) $(+1)$, (HTT) (-1), (THT) (-1), (TTH) (-1), (TTT) (-3)

Total number of possibilities $= 8$

$$f_3(+3) = \frac{1}{8}, \quad f_3(+1) = \frac{3}{8}, \quad f_3(-1) = \frac{3}{8}, \quad f_3(-3) = \frac{1}{8}$$

We consider now four steps, for a walk of four steps,



In general, the probability of taking n1 number of steps to the forward in a total number of N steps is:

$W_N(n_1) = (N!/n_1!(N-n_1)!)\ p^{n_1}\, q^{N-n_1}$

Where $(N–n_1)$ is nothing but number of steps in the back direction. So this one is slightly different from f that we discussed. So, what is p here? p is the probability that the steps is to take in the forward direction and q is the probability that the steps is to take in the back direction. In this special case, means flipping a coin p is equal to q and equals to half, so probability of p and probablity of q they are equal and the value is 1/2.

What we need to do now? Now say, we have taken 3 steps in the forward directions and 1 step in the backward,

So, total number of step = (3+1) = 4

So, $N = 4$ and $n_1 = 3$

So what is $W_4(+3)$ according to the equation we described before?

$W_4(+3) = (4!/3!(4-3)!)\,(1/2)^3\,(1/2)^{4-3} = 4 \times 1/8 \times 1/2 = 1/4 = f_4(+2)$

So, HHHT = $f_4(+2)$

Next, we discuss mean values, how to calculate mean or average value? Suppose we have a set of number, any number you take, suppose 4, 3, 6, 8, 3 and 4. Suppose we have 6 numbers here. If we want to calculate the average of these numbers, what do we do usually?

Average of these numbers, we can calculate very easily like,

Average of these numbers = $(4 + 3 + 6 + 8 + 3 + 4)/6 = 28/6$

Tthis is the one way to calculate.

Another way to calculate average is, another method to calculate average value is = $4\times p(4) + 3\times p(3) + 6\times p(6) + 8\times p(8)$, where, $p(4)$ is the probability of having 4 and so on.

So, probability = $4\times(2/6) + 3\times(2/6) + 6\times(1/6) + 8\times(1/6) = 28/6$

So in both cases we get the same number means we are supposed to get actually. So the average of any quantity we can calculate like number times probability of that number and so on.

Suppose, ‘u' be a variable which can assume M discrete values, what are those values? Like u_1, u_2, u_3 and so on, you get up to u_M and their respective probabilities are $p(u_1)$, $p(u_2)$, $p(u_3)$, and so on up to $p(u_M)$.

So the mean or average value of u, we can write like this, The mean value of u,

$$\bar{u} = \langle u \rangle = \frac{p(u_1) \times u_1 + p(u_2) \times u_2 + \cdots + p(u_M) \times u_M}{p(u_1) + p(u_2) + \cdots + p(u_M)}$$

$$\Rightarrow \bar{u} = \langle u \rangle = \frac{\sum_{i=1}^{M} p(u_i) \times u_i}{\sum_{i=1}^{M} p(u_i)}$$

In most cases, $\sum_{i=1}^{M} p(u_i) = 1$ ⇓ normalisation factor

$$\bar{u} = \langle u \rangle = \sum_{i=1}^{M} p(u_i) \times u_i$$

So what we get? we get mean or average of a quantity u or variable u is sum over probability of particular variable times that variable. Now we will use this one to calculate the mean value of Random Walk Problem.

Calculation of Mean values for the Random Walk Problem

$$W_N(n_1) = \frac{N!}{n_1!\,(N-n_1)!} p^{n_1} q^{N-n_1}$$

The mean number of steps to the forward direction

$$\bar{n}_1 = \langle n_1 \rangle = \sum_{n_1=0}^{N} W_N(n_1) \times n_1$$

$$\Rightarrow \bar{n}_1 = \langle n_1 \rangle = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} p^{n_1} q^{N-n_1} \times n_1$$

Now, $n_1 p^{n_1} = p\left(\frac{\partial}{\partial p} p^{n_1}\right) \Rightarrow n_1 p\, p^{n-1}$

$$\bar{n}_1 = p \frac{\partial}{\partial p} \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} p^{n_1} q^{N-n_1}$$

$$\Rightarrow \bar{n}_1 = p \frac{\partial}{\partial p} (p+q)^N \Rightarrow \text{From binomial Theorem}$$

$$\Rightarrow \bar{n}_1 = pN\,(p+q)^{N-1}$$

For this "flipping of a coin" case $\Rightarrow$ $p+q = 1$ and $p = \frac{1}{2}$

$$\bar{n}_1 = \frac{1}{2} \times N = \frac{N}{2}$$

Average number of steps in the back direction $= N - \bar{n}_1$

$$= N - \frac{N}{2}$$

$$= \frac{N}{2}$$

Total displacement (from the starting point)

$$= \frac{N}{2} - \frac{N}{2} = 0$$

So, when we take a large number of steps then total displacements should be 0, because half number of steps in the forward direction and half number of steps in the backward direction.