Thermodynamics: Classical to Statistical

Prof. Sandip Paul

Department of Chemistry

Indian Institute of Technology Guwahati

Lecture – 12

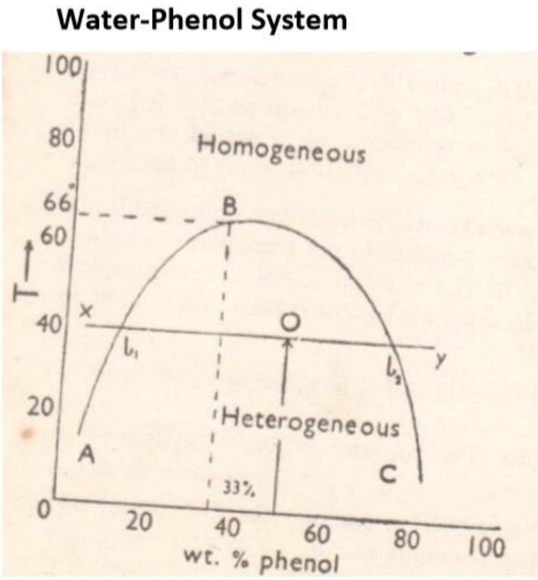
Phase diagram of two component systems

Today we will discuss the phase diagram of two component systems. Two component systems can be of many types like, liquid – liquid phases, liquid – vapour phases, liquid – solid phases, and gas- solid phases. In this course we will consider only the phase diagram of two component system of liquid - liquid phases, so we will consider only liquid - liquid phases.

When a simple alcohol is added to water, these two liquids are completely miscible in any proportion and they form a homogenous solution. But suppose we add water to nitrobenzene or we add nitrobenzene to water, they are not miscible in all proportions, so they are immiscible or partially miscible. So when two partially miscible liquids, suppose A and B, are brought together in appreciable amounts, we get two saturated solutions in two layers, they will form layers because they are partially miscible. So we get two saturated solutions in two layers, one of A in B and another B in A at equilibrium. These two solutions are described as conjugate solutions. Here we will consider systems with liquid-liquid phases, we will consider three different systems.

First we start with water-phenol system. In water- phenol system what we do here actually, we plot temperature versus weight percent of Phenol (Figure 1). Note here, it is convenient to study this kind of system under normal atmospheric pressure. So it is considered that the normal or atmospheric pressure is much, much higher than the vapour pressure of both the components.

At constant 'P'



NOTE
1) It is convenient to study under 'normal' atmospheric pressure

Figure 1

Now if we look this temperature versus weight percent of Phenol as I mentioned here that pressure is constant here, at constant pressure we are dealing with here. So AB curve if you look at this AB curve, it represents the solubility of phenol in water, because we have more water here. And it gives the percentage of phenol dissolved in water at foreign temperature. So if we increase the temperature, solubility increases, you can see that. On the other hand if we add small amount of water in large amount of phenol, we get water in phenol system and this CB curve represents that. So what we discuss now. We infer that AB is the solubility curve of phenol in water. It shows the percentage of phenol dissolved in water at different temperatures. On the other hand when water is added to phenol slowly, small amount of water are immediately dissolved. But when the amount of added water is enhanced or increased, the limit of saturation is reached and water forms a separate layer. So two layers we get. The solubility curve of water in phenol is showed by CB. We can see that if we increase temperature, the solubility of water in phenol increases. Now, we consider a particular temperature, suppose 40°

Celsius. The temperature is given in Celsius in this plot. Suppose for a given temperature of 40° Celsius at point ‘x’, water and phenol are miscible and they form a homogenous solution. So at point x we have only a single phase, P equals to 1 at point x. What is the number of degrees of freedom?

$$F = C – P +1 = 2 – 1 +1 = 2$$

F is C minus P, here it is plus 1 because we have kept pressure constant here. How many components are there? we have two components and one phase and then plus 1 so we get 2, this is by variant.

Now if we fix the temperature at same 40° Celsius and keep on adding phenol starting from point ‘x’, whatever composition we have at point x from that composition if we start adding phenol, What do we get, we reach point l1 and after that, further addition of phenol gives rise to two separate layers. What are those layers? One layer is water in phenol and phenol in water. If we see the left of l1 which present homogenous solutions and the right of l1 indicate the existence of heterogeneous systems of two different phases. What I said is the left of point l1, homogenous solution and the right of point l1 is two phases or heterogeneous system we get. This AB is nothing but the boundary between homogenous and heterogeneous conditions.

Now if we consider right of point l1,

$$F = C – P +1 = 2 – 2 +1 = 1$$

F is C minus P plus 1, here 2 component and 2 phase, so number of degrees of freedom is 1 there. Now point number 5 is, if we see the plot again, similar explanation can be given if we start from point y and keep on adding water at fixed temperature of 40° Celsius means if we star from point y and if we keep on adding water we will reach at point l2 the right side point l2 is nothing but a homogenous system and the left side of l2 is a heterogeneous system of two phases.

Now, any point within the area ABC corresponds to heterogeneous phase and any point outside ABC corresponds to homogenous phase. At 40° Celsius if we take a mixture of 50 percent water and 50 percent phenol and if we shake it and if we allow them to settle, we will get two conjugate solutions, one layer will be having composition as at l1 and the other layer with composition as at l2. So what I said is, at 40° Celsius if we shake a mixture of 50 percent water and 50 percent phenol and then allow them to settle, we get two conjugate solutions, one layer having composition as at l1 and another layer having composition as at l2 and that is represented by O. Suppose we take a composition of 33 percent of phenol and 67 percent of water and we shake them, then allow them to settle. We get two layers, when temperature is below 66° Celsius, that what we had discussed is that dotted line, so temperature is below 66° C. Above 66° Celsius we get a homogenous solution. So what I wanted to say here is it is evident that any temperature above that of point B, water and phenol are completely miscible in all proportions. Although, we consider 33 percent phenol and 67 percent phenol, it take any proportion and you keep on increasing the temperatures above 66° Celsius these two liquids are completely miscible with each other in all proportions. The temperature above which the complete miscibility in all proportions takes place is called or is known as upper consolute temperature or critical solution temperature or CST. The temperature above which complete miscibility in all proportions takes place is known as upper consolute temperature or critical solution temperature. If for water phenol system, the value of CST is 66° celsius. Now we have considered one system for which we got upper consolute temperature. Is it possible to have a lower consolute temperature, means the temperature below which two liquids will we miscible with each other? Yes, there is a system we are going to consider next.

Next we consider water-triethylamine system. Here, again we plotted temperature verses percentage of triethylamine at constant pressure (Figure 2). So what we observe here like before we can draw a few conclusions from the above phase diagram.

Water-Triethylamine System

At constant 'p'

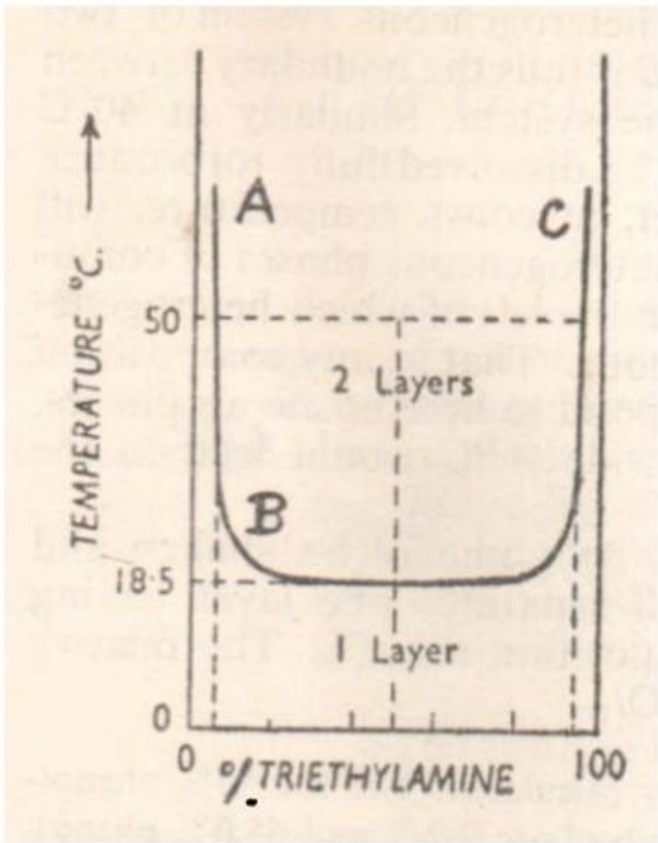


Figure 2

i) The curve AB is the solubility curve of triethylamine in water.

ii) CB is the solubility curve of water in triethylamine.

iii) In both cases the solubility decreases with increasing temperature.

iv) The solubility curves becomes almost horizontal at about 18.5° Celsius and they practically merge at this temperature.

v) Now, as in previous example like water-phenol example, any point within the area ABC corresponds to heterogeneous system. We get two layers inside ABC.

vi) Any point outside ABC corresponds to homogenous system.

vii) Most importantly below the temperature of that of point B, the two liquids are miscible in all proportions.

viii) This system has a lower consolute temperature or critical solution temperature.

So this system means this water triethylamine system, it has a lower consolute temperature in this case 18.5° Celsius. So far we have considered two systems, for which, in case of first system we have obtained the upper consolute temperature and for water triethylamine have seen that there is a lower consolute temperature.

Now, can we have a system which is having both upper and lower consolute temperatures? Yes, that is what we are going to discuss now. So we consider now water-nicotine system. Again we consider at constant pressure ‘p’. So we plotted temperature versus percentage of nicotine here (Figure 3).

At constant ‘p’

Water-Nicotine System

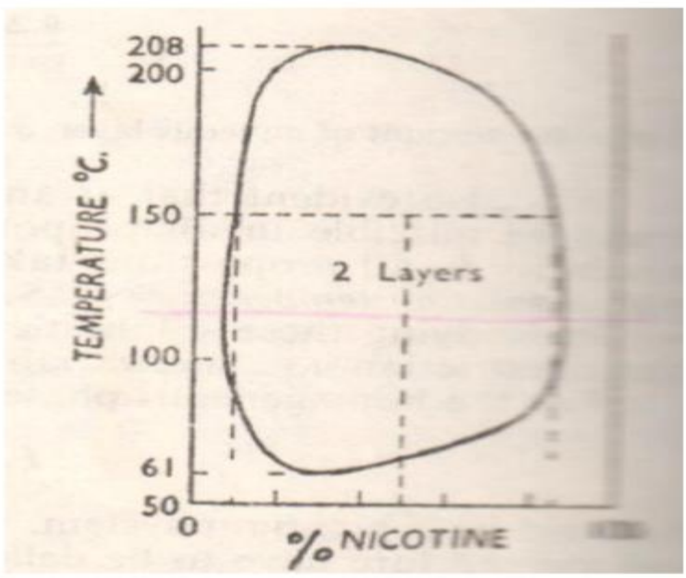


Figure 3

i) Here what we see, we can summarize like the mutual solubility curve means water in nicotine and nicotine in water is a closed one having both an upper critical solution temperature and a lower critical solution temperature. Above 208° Celsius and below 61° Celsius, water and nicotineor liquids are completely miscible in all proportions. These are upper critical solution temperature and lower critical solution temperature.

ii) In between these two temperatures with appreciable amounts of the components, we get two conjugate solutions. Within the curve, within the closed area we get two layers, above 208° Celsius and below 61° Celsius, water and nicotine are completely miscible with each other.