

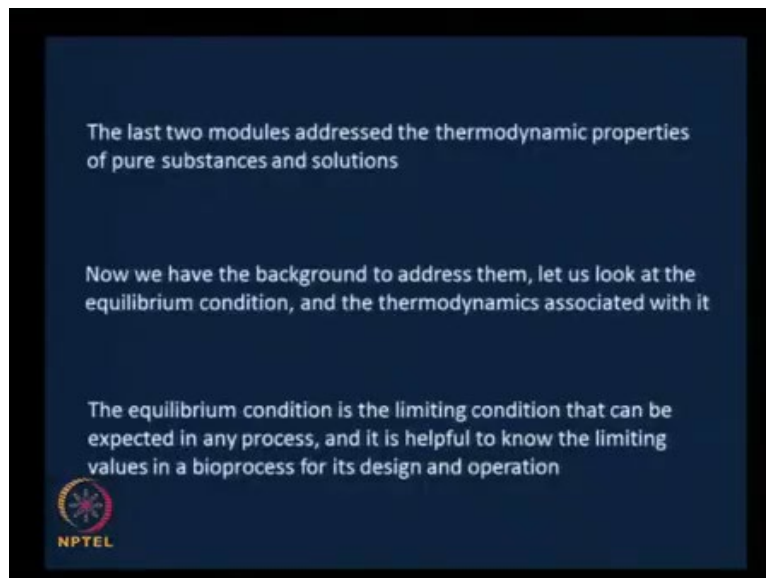
**Thermodynamics for Biological Systems:  
Classical and Statistical Aspects  
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**Lecture – 37  
Criteria for Phase Equilibrium**

Welcome!

In this lecture, let us begin module number 5. Module number 5 is on phase equilibria. We all know what phases are – the 3 phases that we are looking at in this particular course are the solid, liquid and the gas or the vapour phase. We are going to look at the equilibria that concerns these phases in this particular module.

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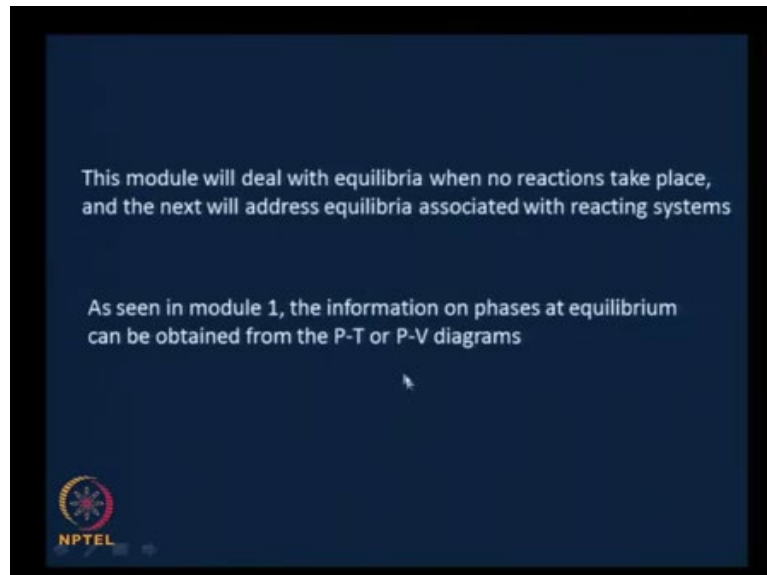


The last two modules, you know, we had looked at pure components first and then the solutions. The last two modules addressed the thermodynamic properties of first, pure substances that was module number 3. Then module number 4, looked at solutions or mixtures, which are essentially the things that arise when you put a lot of pure substances together, a minimum of 2 pure substances together. Now, we have the background to address them that is the pure substances as well as the mixture of pure substances.

It is natural for us to look at the next aspect, which is the equilibrium condition, and of course, the thermodynamics associated with the equilibrium condition. A little while later, I will tell you what equilibrium actually is, what is the nature of equilibrium, and so on.

Very briefly, now, let me tell you that the equilibrium condition is the limiting condition that can be expected in any process. Any process is expected to ultimately reach equilibrium, and it is helpful to know the limiting values in a bioprocess for its design and operations. We just leave a process alone, it might attain equilibrium may be in a few milliseconds, microseconds, or may be over years. But, it is good to know the limiting values, so that we can design, keeping that in mind ... knowing that is the maximum that we can achieve. And whatever we are going to actually achieve would be some fraction of what is maximally achievable.

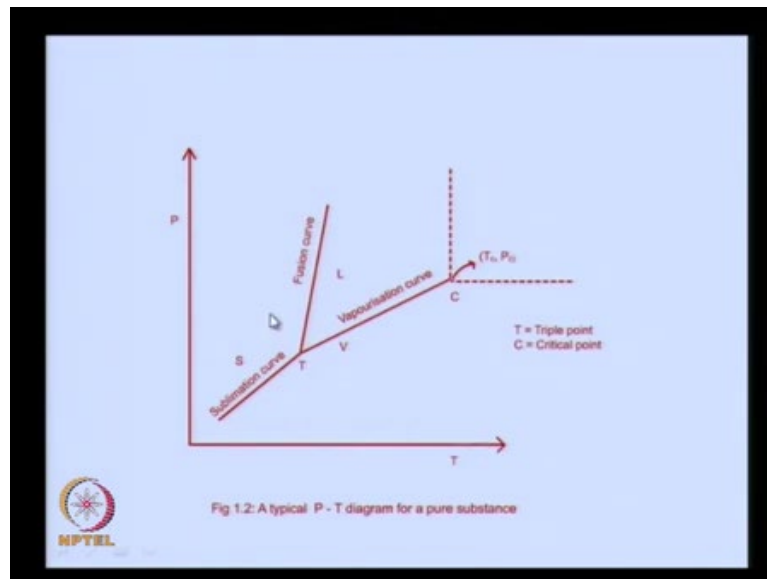
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This module will deal with equilibria when no reactions take place, and the next module, module number 6 will address equilibria associated with reacting systems. Therefore, in this particular module, we will not consider any reactions at all. Let us go back a little bit, to familiarize ourselves or recall whatever we did in module 2, because it becomes necessary here in the context of phase equilibria.

We saw in module 1 that the information on phases at equilibrium can be obtained from either the pressure verses temperature diagram or the pressure verses the specific volume diagram. If you recall those figures.

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We will take a look at them again here. This is the P-T diagram. Of course, this is only for a pure substance, which mean only one type of substance. We need to interpret this as we saw earlier, as the space consisting of certain values of temperature and corresponding values of pressure. This is the sublimation curve, which is essentially a demarcating line between the region where the solid exists and the vapour exists.

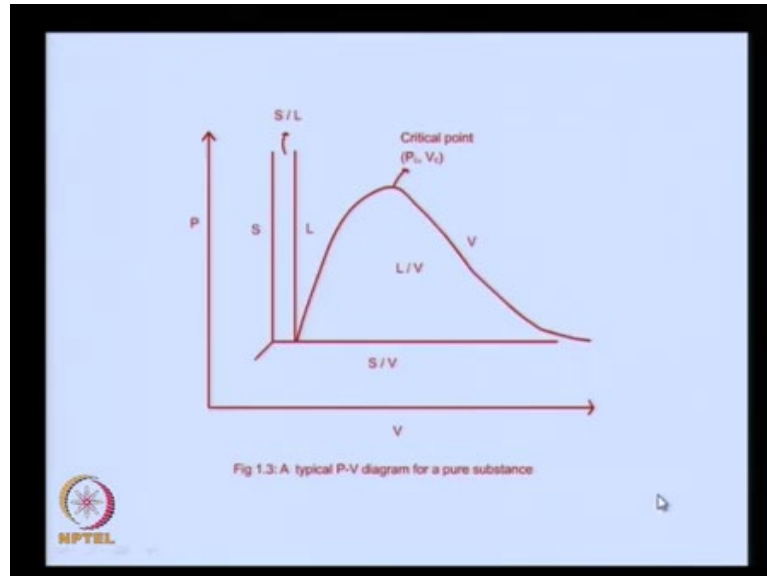
On this line, you expect the conversion from the solid phase to the vapour phase or the gaseous phase. This is the fusion curve, which is the demarcating line between the solid phase and the liquid phase of one substance, one pure substance. Therefore, along the fusion curve, we can expect the transition. Which means that if a substance is going from the solid to the liquid, that can happen only along these combinations of temperature and pressure – you know ... x axis ... y axis... so, (T, P) is each point here – that can happen only along the fusion curve.

Similarly, this is the vaporization curve, which is a transition or a limiting line between the liquid and the vapour phases. Therefore, if a liquid becomes a vapour, it has to happen under these conditions, or these combinations of temperature and pressure.

And we have also seen for completeness sake that this is the critical point, ... beyond which the critical phase exists; which means above the critical pressure and above the critical temperature, we have the critical phase, which is very interesting in itself. But, we will not address that in this

particular course. Therefore, in this course we will essentially look at solid, liquid and vapour phases and the demarcating regions.

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In contrast to this, if we look at pressure versus the specific volume diagram, for a pure substance, we saw that these combinations of specific volume and pressure ... would result in a solid. These combinations of specific volume and pressure would result in a liquid, and these values of specific volume and pressure would result in a vapour. There are regions – unlike the P-T diagram, where they were lines, combinations of temperature and pressure, where the transition took place – here, we have regions over which transitions from one phase to another phase take place.

For example, this region ... is the region over which the transition from the solid to the liquid phase takes place. This is the region over which – the dome – is the region over which the transition from the liquid to the vapour phase takes place and so on.


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A  $P - T$  or a  $P - V$  diagram provides the information on the phases that exist at particular conditions of temperature and pressure, typically for a pure substance

For example, **at atmospheric pressure**,  $H_2O$  is a gas above  $100\text{ }^\circ\text{C}$ , a liquid between  $0$  and  $100\text{ }^\circ\text{C}$ , and a solid below  $0\text{ }^\circ\text{C}$

At  $100\text{ }^\circ\text{C}$ , liquid and gas can co-exist  
At the triple point ( $\sim 0\text{ }^\circ\text{C}$  for water), all the three phases coexist

When we have a mixture of pure substances (say  $H_2O$  and air; note that air consists of  $N_2$ ,  $O_2$ ,  $CO_2$ , etc.,), the behavior would be different



We had already mentioned this: a  $P$ - $T$  or a  $P$   $V$  diagram provides the information on the phases that exist at particular conditions of temperature and pressure, typically for a pure substance.

For example, at atmospheric pressure ... you know, we said that only at a certain conditions of pressure, temperature and specific volume, do these transitions exist ... at atmospheric pressure, 1 atmosphere pressure,  $H_2O$  or water is a gas above 100 degree C, a liquid between 0 and 100 degree C, and a solid below 0 degree C.

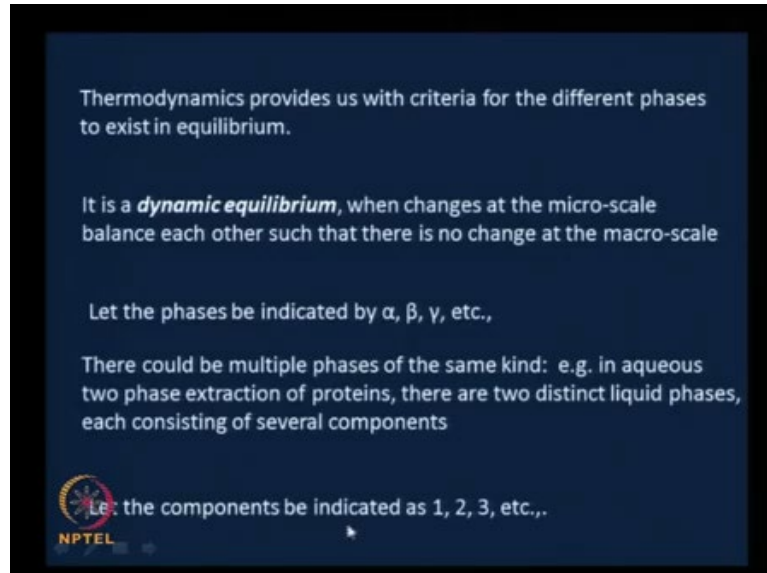
At 100 degree C, you know, at that particular temperature, liquid and gas of  $H_2O$  can co-exist. We are all talking about atmospheric pressure here. At the triple point, which is about 0 degree C for water, all the 3 phases such as solid liquid and vapour – they co-exist.

Now, we need to distinguish this pure substance from what we normally come across, which is the mixture of pure substances. I have given this example before, and just to drive home the point clearly, let me give it again. When we have a mixture of pure substances say water and air, this is something that we find around us all the time, you know there is air and there is some water vapour in it.

If we note this, the air it itself consists of different species, nitrogen, oxygen, carbon dioxide and so on. Therefore, this mixture of water vapour and air contains all these plus water vapour. When we have such things the behavior of course, is going to be different. Therefore, we should not make the error of extending the phase diagram for a pure substance to that for mixtures. And it

happens without us realizing; that is a reason why I am making the point here especially in the case of water and air. Please note this.

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Thermodynamics provides us with the criteria for different phases to exist in equilibrium. It tells us a priori when they will be in equilibrium, and that is the power of thermodynamics.

It is at dynamic equilibrium, when changes at the micro scale balance each other so that there is no change at the macro scale. You know at the equilibrium conditions, things do take place, processes do take place. But, the rate of the process in one direction equals the rate of the process in the other direction at the micro scale. And therefore, both the rates cancel each other, and net at the macro scale, we do not find any major difference.

What I mean by this is: consider the evaporation of water. When the liquid water becomes or gets into the vapour phase, there is movement of water molecules from the liquid to the vapour. And let us say under a given set of conditions, that takes place at a particular rate. Here there is no air, by the way. Just water and vapour – a pure substance. So, the liquid water becomes vapour. At the same time you know there is water vapour there, some of those molecules may not have enough energy and they will get back to the liquid phase.

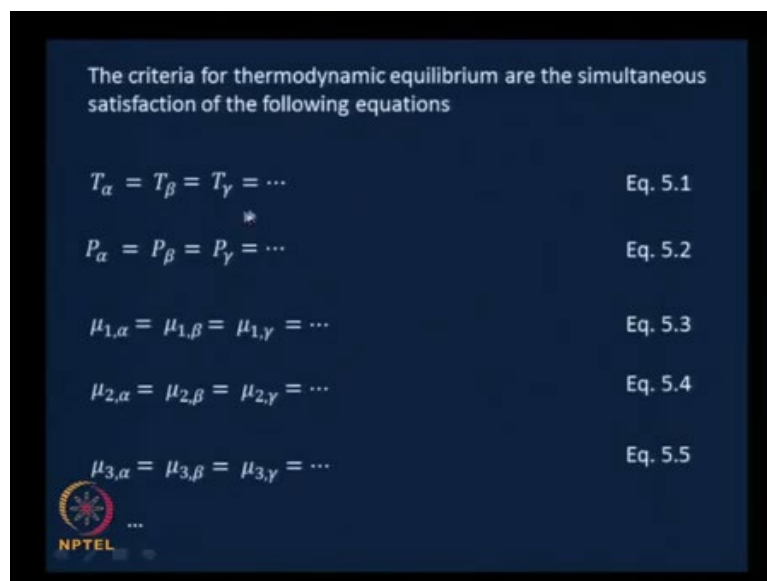
So, there is a rate at which liquid water becomes gaseous water, and there is a rate at which the gaseous water becomes liquid water. What happens at equilibrium is that these two rates match.

That is all that happens. There is still continuous motion or movement of liquid water to vapour water, and there is still motion from the vapour phase to the liquid phase. These two rates match, and that is why we call it a dynamic equilibrium.

For the purposes of this course, let the phases be indicated by alpha, beta, gamma, and so on. Might need more and in a minute we will see why. There could be multiple phases of the same kind; that is why we need more.

For example, we all know that or we may know that proteins are purified, or extracted, through a process called aqueous two phase extraction, where we have two liquid phases, two aqueous liquid phases. So you can call one, alpha, the other one, beta, and so on and so forth. And each of those phases consists of several components. Let the components be indicated as 1, 2, 3 and so on.

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The criteria for thermodynamic equilibrium are the simultaneous satisfaction of the following equations

$$T_{\alpha} = T_{\beta} = T_{\gamma} = \dots \quad \text{Eq. 5.1}$$

\*

$$P_{\alpha} = P_{\beta} = P_{\gamma} = \dots \quad \text{Eq. 5.2}$$
$$\mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \dots \quad \text{Eq. 5.3}$$
$$\mu_{2,\alpha} = \mu_{2,\beta} = \mu_{2,\gamma} = \dots \quad \text{Eq. 5.4}$$
$$\mu_{3,\alpha} = \mu_{3,\beta} = \mu_{3,\gamma} = \dots \quad \text{Eq. 5.5}$$

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Now, comes the criteria that thermodynamics gives us for thermodynamic equilibrium. And for thermodynamic equilibrium the following equations must be simultaneously satisfied.

The temperature of the alpha phase must equal the temperature of the beta phase must equal the temperature of the gamma phase and so on, which means that the temperature of all the phases has to be equal.

$$T_{\alpha} = T_{\beta} = T_{\gamma} = \dots$$

That is the first condition for thermodynamic equilibrium, and we will call that equation 5.1.

Secondly, the pressure of the alpha phase, must equal the pressure of the beta phase, must equal the pressure of the gamma phase, and so on. In other words the pressure of all the phases in equilibrium must be the same.

$$P_{\alpha} = P_{\beta} = P_{\gamma} = \dots$$

Or, in other words, only if the pressures are the same can we call the phases to be in thermodynamic equilibrium; we will call that equation 5.2.

Also, remember the chemical potential that we talked about. The chemical potential of component 1 in the alpha phase, note this, we are talking of a chemical potential of a certain component. And certain component in the alpha phase,  $\mu_{1,\alpha}$ , must equal the chemical potential of the same component in the beta phase that must equal the chemical potential of the same component 1 in the gamma phase, and so on and so forth.

$$\mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \dots$$

In other words, the chemical potential of a certain component must be the same in all the phases that are present at equilibrium. We will call this equation 5.3.

The other things are quite easy to see. The chemical potential of second component must be the same in all the phases:

$$\mu_{2,\alpha} = \mu_{2,\beta} = \mu_{2,\gamma} = \dots$$

We will call this equation 5.4.

Same thing continued ... let me write one more and put dot dot dot later,

$$\mu_{3,\alpha} = \mu_{3,\beta} = \mu_{3,\gamma} = \dots$$

and must be equal to the  $\mu_3$  in each of the other phases, we will call this equation 5.5 and so on. ... We will have the number of these equations being equal to the number of components that are present in this system, which consists of phases in equilibrium.



To repeat, the temperatures have to be the same across the phases. The pressures need to be the same across the phases, as well as the chemical potential of each component must be the same across phases. These are the conditions for equilibrium. We can use it both ways; we can use it to check whether the equilibrium is achieved, we can use it to predict when equilibrium will be achieved.

See you in the next class.