Hello students, welcome to this course Heat and Thermodynamics and Properties of Matter and Acoustics. This is section one Heat and Thermodynamics. The unit is Second Law of Thermodynamics and the name of the module is Clapeyron Latent Heat Equation and Its Applications. I am Yatin Desai, Assistant Professor in Physics, Chowgule College, Margao – Goa.

Outline of this module is Clapeyron Latent Heat Equation and Its Applications

At the end of this module, you will be able to derive Clapeyron first latent heat equation, derive Clapeyron second latent heat equation, apply latent heat equation to understand the effect of change of pressure on the melting point and on the boiling point. You will be also able to explain why the saturated steam has a negative specific heat.

Clausius – Clapeyron or the first latent heat equation: Consider a unit mass of a gas taken through Carnot cycle working between temperatures T degrees K & (T – dT) degrees K, where both the temperatures are below the critical temperature of the substance. ABCD & the curve EFGH are two isothermals corresponding to temperatures (T – dT) degrees Kelvin and T degrees Kelvin respectively. This is shown in this figure. Let FI & GJ be the adiabatic curves drawn through F and G to meet BC. If dT is very small, the difference is BI and JC can be neglected. Now at F, the substance is entirely in the liquid state and at G it is just completely in the vapor state. The amount of heat taken in by this substance in passing from F to G, that is, in passing from the liquid phase to the vapor phase is L; that is the latent heat.

The work done by the substance in one cycle can be expressed in two ways: The first one is work can be calculated by using the formula efficiency multiplied by heat taken in at higher temperature. Similarly, the work can also be calculated by considering the area of the loop.

From the theory of Carnot cycle, efficiency is eta which is equal to (T1 – T2) / T1. Here we have T1 as T and T2 as (T minus dT). Therefore, eta is T minus of T minus dT divided by T. Here T gets cancelled and we get eta as dT by T. Now as per the first way of calculating the work done, we have work done as efficiency multiplied by the heat absorbed. OK, so this is the efficiency. Therefore, we write W equals (dT by T) multiplied by L. This is the one way of calculating the work done. This is equation number (1). Now let us calculate work done again by using the second method that is by considering the area of the loop. And here we have to consider the area of the loop FGJI and if dT is very small then it is equivalent to a rectangle which is marked as FGNK in the previous diagram. So, it is FGNK, FGJI if dT is very small it can be taken as this rectangle FGNK. Therefore, the work done of this is length into breadth. OK, so this is dP which is the pressure axis and these are the ordinates on the volume axis V2 and V1. So, it is V2 minus V1. OK, this is because that length FG is V2 minus V1 and FK is change in the pressure because that is the pressure axis.

Since equations (1) and (2) are both the equations for the same work done, we can equate them as dP times (V2 minus V1) = (dT by T) into L. Or dP by dT is equal to L / T times (V2 – V1). This is equation #3. This is called as the Clausius – Clapeyron equation or the first latent heat equation. Equation 3, which is derived for the liquid and vapor phases, can also be applied to the change of phase from a solid to a liquid state. In case of a change of phase from liquid to vapor, V1 corresponds to the volume of the liquid phase and V2 correspond to the volume of the vapor phase. But in case of a change of phase from solid to a liquid state, (V1 corresponds to) V1 and V2 are the specific volumes of the substances in the solid and liquid state, respectively.

If the first latent heat (equation) is applied to the melting point of a solid at the melting point. In case of the substance, such as ice, that contract on melting that is V2 is less than V1. In that case, dP by dT is negative, hence melting point of solid or the freezing point of liquid decreases with increase in pressure. Next, in case of this substance, that expand on melting that is V2 is greater than V1, the melting point increases with increase in pressure. Similar considerations apply to the change of boiling point with pressure in the case of phase from liquid to the vapor state. In almost all such cases, the boiling point increases with pressure.

Second Latent Heat Equation: Consider a unit mass of gas substance taken in Carnot cycle between temperatures T & (T – dT) as in the previous case. Starting from point F, at which the substance is entirely in the liquid state, it may be taken as in a cycle represented by FGC&B, as shown in this figure, FGC&B. If dT is very small, we can assume that the parts of the cycle GC and BF almost coincides with the adiabatic GJ and IF respectively.

Let L & (L – dL) be the latent heat of vaporization at T degrees Kelvin and (T – dT) degrees Kelvin respectively. Starting from the point F, (the heat absorbed) taken is along FG that is L. So, heat absorbed along FG is L. The heat given out along GC is C2 times dT. So C2 here is the specific heat of saturated vapour. The heat given out along CB is (L – dL) and heat absorbed along BF is C1dT, where C1 is the specific heat of the liquid and therefore the net heat absorbed in a cycle is Q = L – C2dT – (L – dL) plus C1dT. Here, we can cancel this L and write rest of the terms as dL plus (C1 – C2) times dT. This is equation #1. This is equal to the work done per cycle. that is W equals dL plus (C1 – C2) times dT. The heat taken in at higher temperature is L. The expression for the efficiency of Carnot's engine is eta equal to dT by T. The work done per cycle is eta times heat taken in at higher temperature, that is W equals dT by T times L This is equation #2. Equating right hand sides of equation (1) and (2), we get dL plus (C1 – C2) times dT equal (dT by T) * L. Or (dL by dT) minus (L by T) = C2 minus C1. This is equation #3. This is the second latent heat equation, or Clausius latent heat equation.

In case of water at 100 degrees C, (dL by dT) = - 0.64 and L = 540 calories. T is say 370 degrees Kelvin and C1 = 1 Calory. Therefore, C2 is (1 – 0.64) – (540 by 373). We get it is minus 1.087 calories. Thus, the specific heat of saturated steam at 100 degrees C is negative.

Now explanation of this negative specific heat of saturated steam. Consider one gram of saturated steam at 100 degrees C. The specific heat is the quantity of heat required to raise the temperature by 1 degree C, that is from 100 degrees C to 101 degrees C. When the temperature is raised, the steam become unsaturated. To keep it saturated at 101 degree C, it has to be compressed and in this process the temperature rises above 101 degrees C. Therefore, heat has to be taken out of steam to keep it saturated. The heat taken out happens to be greater than heat supplied to steam in raising its temperature from 100 degrees C to 101 degrees C at the same time keeping it saturated. Therefore, the specific heat of saturated steam at 100 degree C is negative.

These are the references for this module.

Thank you.