Basic Thermodynamics

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Lecture - 18

Properties of Pure Substances -Ideal Gases

Good morning. We are discussing about the properties of pure substances for last few classes, phase diagram.

Today, we will be closing that topic by discussing one aspect of this which is known as Clausius-Clapeyron equation. We have recognized that saturation states are specified by the couple of pressures and temperatures, both for transformation from liquid to vapor and from Solid to liquid. What is the relationship between these two so that one knows the pressure can automatically know the temperature, based on which the pressures and temperatures are determined and tabulated. For an example, in steam table for water, we know that when saturation pressure is fixed temperature. For example, if it is one atmospheric pressure then the saturation temperature is 100 degree Celsius. Similarly, if the pressure is ten atmospheric then what is the saturation temperature?

What is that relationship based on which the values are tabulated was given by two scientists Clausius and Clapeyron. So, this we will discuss today.

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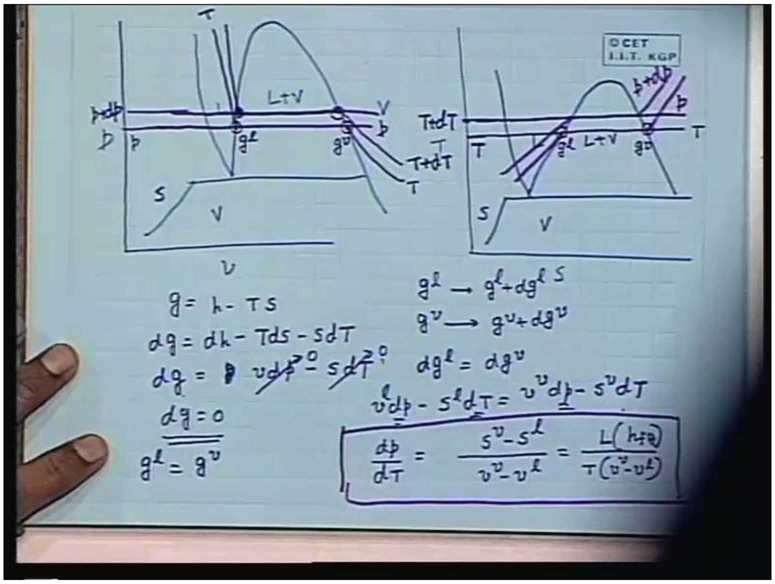

Let us again recall the pv diagram. This is the p and v as usual. We are bothered only on the liquid vapor, it does not matter. We can consider this for solid, liquid also. Similar thing will apply and this is the Ts diagram; I am drawing it like this. So this is liquid, liquid plus vapor, this is the triple point line Solid, vapor, Solid.

If we denote the pressure, for example, at the given pressure, this is the constant pressure line. So, this is the pressure. The saturation temperature for this pressure is the isotherm which passes through this, coincides with this pressure line in the vapour dome; this is the isotherm. If this be the pressure the corresponding temperature is this isotherm. Similarly, here also, if these be the isotherm, let these be the isotherm T. What is the pressure? Corresponding pressure is this one, this is p; that means, p and T, here represents the saturation pressure and temperature. Now, what are the relationship between this p and T? That means if we increase the pressure, the temperature will increase. (Refer Slide Time: 03:05 to 03:46)

Let us recognize one thing that in this type of phase change, the specific volume changes as this change of phase takes place the specific entropy changes. Similarly, the specific enthalpy changes which is found in hs diagram. But now, if was define the Gibbs function, specific Gibbs function, according to his definition g is equal to h minus Ts. If we differentiate dg then we get dg is equal to dh minus Tds minus sdT.

Dh minus Tds is vdp minus sdT . This relationship we also used earlier, just specific this function. That is why it is v specific volume, s specific entropy. During this phase change, since pressure and temperature remains constant which means dp and dT is 0. Therefore, dg is 0.

Another thermodynamic property that is the Gibbs function, or the specific Gibbs function that remains constant along with pressure and temperature during a phase change; change of phase from one state of matter to other state of matter. This is one very important conclusion. If this is so then we can tell that this if we denote it as Gibbs function of the liquid, and if we denote it as Gibbs function of the vapor, since we are using g, we are not using f and g; otherwise, it will be confused.

For all properties, we have seen even in this steam table, the subscript f is used for the liquid and subscript g is used for the tri-saturated vapor. But here we are using g itself as the specific Gibbs function. I am using superscript l for the liquid and that for the vapor. So, from this relationship we can take that at a particular pressure and the corresponding temperature, this g of l of liquid state is equal to g of v that is vapor state.

Consider a small infinite small change in temperature. To find the relation, we have to do like that an infinite small change in temperature or pressures. Here, the pressure first; that means, if this is P all the time this change of pen. So, this is p and this is p plus dp. Similarly, the isotherm which passes through this that means if the saturation temperature also suffers a small change that means T plus dT. Similarly, the isobar which passes through this coincides with this constant pressure thing; this isobar is p plus dp. That means, we change the pressure from p plus dp. What is the corresponding change in the temperature?

Let this be T plus dT. Let us consider that the Gibbs function in the liquid phase, as a change from g l to g l plus dg l and the vapor phase Gibbs function changes from this to g v plus dg v. Again, they are equal, because at this point, this g and this g (Refer Slide Time: 07:34) that means Gibbs function for the saturated liquid and dry saturated vapor are equal; that means these two are equal. Therefore, dg l which simply means that change in the Gibbs function for the liquid state will be same as that for the vapor state so that they again become equal if the states are saturation states.

So how to write then, okay you keep this please Sorry you keep this okay okay okay. I will write okay.

Therefore, we get dg l is dg v. If we write this expression, dg l is vdp l or dp. dp is the same minus v l minus s l dT is equal to. We can write for this following this equation v of v dp minus s v dT. This dp, dT is not 0. This dp, dT indicates a change in pressure and temperature like this. There is a change in pressure and temperature for which there is a change in the liquid phase Gibbs function which must follow this general thermodynamic relation. That means dg is equal to v dp minus sdT. Whenever there is a change in pressure and temperature, there will be a change in Gibbs function. Therefore, dg is this and dg v is this.(Refer Slide Time: 09:04)

From which we get, dp by dT will be equal to s v minus s l divided by v v minus v l. This s v minus s l is the change in the entropy, specific entropy for change of phase which can be written as latent heat divided by the saturation temperature into v v minus v l. Sometimes, the latent heat may be written in terms of the enthalpy change hfg. Sometimes, it is neither by L nor by hfg. This is one of the very important property relations.

Sorry not property relations, I am extremely Sorry. This is one of the very important relations not property relations. I am Sorry. dp by dT that is the change in pressure with respect to temperature is L by T into v v minus v l.

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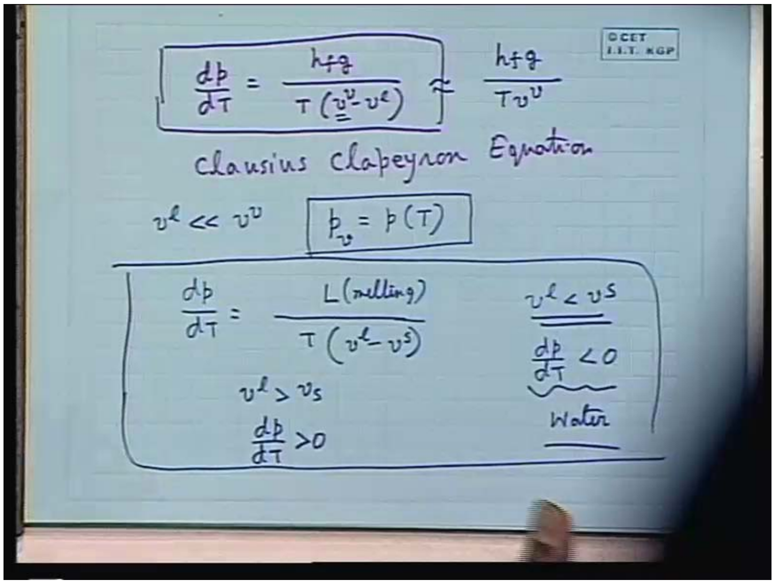
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$$\boxed{\frac{dp}{dT} = \frac{h_{fg}}{T(\underline{v^v} - v^l)}} \approx \frac{h_{fg}}{T v^v}$$

Clausius Clapeyron Equation

$v^l << v^v$ $\boxed{p_v = p(T)}$

$$\frac{dp}{dT} = \frac{L(\text{melting})}{T(v^l - v^s)}$$

$v^l > v_s$

$\frac{dp}{dT} > 0$

$\underline{v^l < v^s}$

$\frac{dp}{dT} < 0$

Water

Again, I write this expression. Therefore, we get is that dp by dT is equal to L or hfg divided by T. That is the change in this specific entropy. This equation is known as Clausius-Clapeyron equation. Therefore, this equation gives the relationship between the saturation pressure and the saturation temperature. From this differential equation, we can integrate, but integration is not very easy. This is because of the fact. This v v is a function of temperature usually; v l is very small with respect to v v. Sometimes, we can neglect this, because the specific volume of the liquid is very small compared to that of the dry saturated vapor.

So, hfg is also a function of temperature. So, until and unless we know the functional relationship of hfg v v with temperature or pressure, we cannot integrate it. Therefore, this equation can be integrated, provided we know this variation. Usually, these variations are given in terms of empirical equations so that one can integrate this equation and express an explicit functional relationship of p with respect to temperature. This is the relationship of the saturation pressure corresponding to the saturation temperature. This pressure is sometimes known as vapor pressure; vapor pressure versus temperature relation. Sometimes, we tell colloquially that what are the vapor pressure temperature relations? What is the relationship between the saturation pressures to its corresponding saturation temperatures at which a phase change takes place?

In case of liquid vapor transitions, v v is always higher than v l, hfg is a positive quantity, T is a positive quantity, dp by dT is positive. Pressure changes with the temperature.

In case of Solid, liquid transitions that means melting or freezing this equation can be written as hfs that means sf. I can write latent heat for melting usually this nomenclature is used. In that case, v v will be v l that is the final phase minus this is the initial phase that means v s. Now, this will be positive provided on melting, this specific volume increases. So, for the substances where melting increases the specific volume; that means, the system expands on melting. dp by dT is positive; means an increase in pressure will increase the saturation temperature.

For substances where v l is less than v s; that means, this system contracts on melting. In that case, dp by dT is negative. An increase in pressure will reduce the saturation temperature. What happens in case of water?

In this case, dp by dT is negative and when v l is greater than v s, dp by dT is positive. So, this is the case for water. In case of Solid, liquid just I give this example, but we are not much bothered on this aspect. We are only concerned with the boiling, where the vapor is transformed into liquid. This is so small. Sometimes, it can be written as hfg by Tv v. For all liquids, v v is much much higher than the v l.

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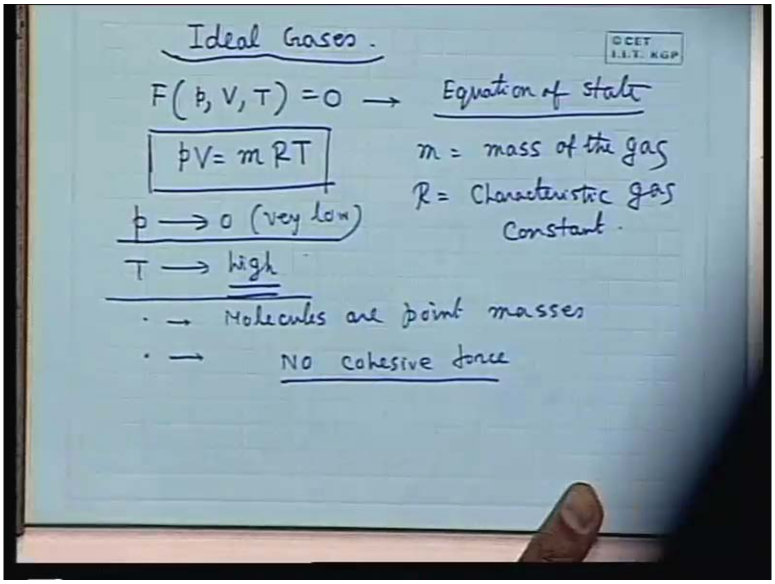

Ideal Gases.

$F(p, V, T) = 0 \rightarrow$ Equation of state

$\boxed{pV = mRT}$

m = mass of the gas

R = Characteristic gas constant.

$p \rightarrow 0$ (very low)

$T \rightarrow$ high

- → Molecules are point masses
- → No cohesive force

Now, I come to the very simple old and known things, ideal gases.

This will be mostly the recapitulation of the things which you had read at your school levels with addition of few materials but brushing of your concept.

For any compressible system, a functional relationship between pressure, volume and temperature are the three fundamental properties of a system. All these three are directly measurable and sensible also. We can sense pressure and temperature. A functional relationship between these three properties is known as equation of state.

An ideal gas if we ask what is the definition of an ideal gas?

It can be defined in various ways, but all the definitions are same. One is a corollary of the other. We can start from the equation of state point of view. An ideal gas is a gas which obeys this relationship as the equation of state at all pressure, volume and temperatures. At any state points, the relationship will be pV is equal to m RT, where m is the mass of the gas and R is a constant known as characteristic gas constant whose value is constant for a particular gas, but varies from gas to gas.

This relationship is very simple relationship and has to be valid at all state points. It has been found in practice that all the gases in reality do not exactly obey this equation; this functional relationship between pv and T. Gases only obey with a fair accuracy. This relationship, when its pressure is extremely low, p tends to 0, very low or temperature is extremely high. I will not write infinity. This will be odd, because at very high temperature, the gases are ionized and are converted into another state known as plasma state which is not a neutral state, ionized state. So, at very high temperature, if the gases are highly superheated or rarefied, for example, we consider air is at a tremendous superheated condition or a rarefied condition. I expressed this thing earlier, while discussing the phase diagram what is the superheated or rarefied state.

Air in a superheated state, is a high degree of superheat, because if we consider air at the atmospheric pressure then if we think its temperature, for example, today, just now, I have been told that temperature is 23 degree Celsius. But what is the temperature at which air is condensed or liquid air boils up at one atmospheric pressure. Though liquid air is not a pure component, it consists of nitrogen and oxygen, but their boiling points are very close.

We can take a rough idea that it is some minus170 degree Celsius or so. Approximately, how much degree of superheat it is? It is at a highly superheated condition corresponding to its existing pressure. At the same time, if we consider the 23 degree Celsius as the existing temperature at which the air can be liquefied. Yes, it can be liquefied.

If we compress the air and to do that we have to compress the air up to 50 or 100 atmospheric pressure or even more so that air is at a rarefied state. Therefore, at a very superheated or rarefied state, a gas obeys that means when the pressure is very low and temperature is very high obey the equation of state. This is experiments, but theoreticians on the other hand have derived this equation from kinetic theory of matters, provided we are allowed to assume certain postulate. They have to make certain assumptions. What are those assumptions?

Number one assumption is that, I am not writing all these things it is boring. Molecules are point masses that they do not have any volume. The volume of the molecules is neglected in comparison to the volume of the geometrical system; that is number one.

Number two is that no cohesive force. Cohesive force is the force of attraction or repulsion between the molecules of the same kind. In fluid mechanics, we have learnt that there are two types of forces. Intermolecular forces, there exists, one is the force of cohesion which is the intermolecular forces; forces of attraction and repulsion in between the molecules of the same kind. For a given system which comprises a large number of molecules, there are internal forces, attraction and repulsion forces of the molecules which largely depend upon the molecular density. The free path of the molecule, the distance between the two molecules are in main free path. How do did we define statistical average of the distance between two successive collisions? Therefore, these intermolecular forces are known as cohesive force.

Another force is the adhesion force for that adhesion which is the intermolecular forces between the molecules of the two different kinds between two different systems. So, the molecular cohesive forces or molecular attractive or repulsive forces are 0, because of which molecules are capable of moving in a straight line rectilinear motions. So, if we assume these things then from the kinetic theory of matter, one can derive this relationship pV is equal to m RT.

The kinetic energy of the molecule is a function of temperature which gives the concept of temperature from statical thermodynamics which was given by Maxwell and Boltzmann. This is beyond the scope of this classical thermodynamics which we are dealing with now.

If we know this information that is sufficient that an ideal gas from kinetic theory of matter had these assumptions, that the molecules do not have any volume and the internal forces between the molecules; that is, cohesive forces in molecules are absent. Then molecule moves perfectly in a straight line; the rectilinear motion. One can reduce this, but we are not much bothered of these assumptions in the kinetic theory. We are only bothered in classical thermodynamics with this equation pV is equal to m RT.

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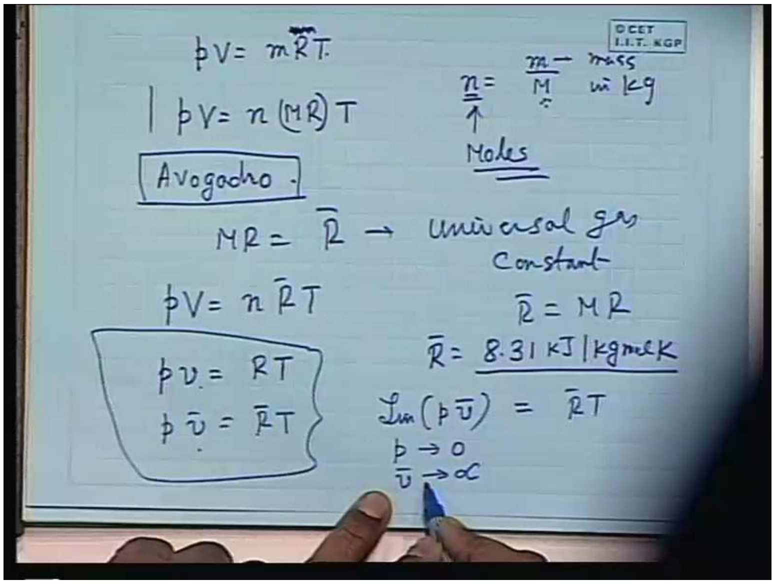

$pV = mRT$

$pV = n(MR)T$

$\underset{\substack{\uparrow \\ \text{Moles}}}{n} = \frac{m}{M}$ m — mass in kg

$\boxed{\text{Avogadro}}$

$MR = \bar{R} \rightarrow$ universal gas constant

$pV = n\bar{R}T$

$\bar{R} = MR$

$\bar{R} = \underline{8.31 \text{ kJ}/\text{kgmol K}}$

$pv = RT$

$p\bar{v} = \bar{R}T$

$\lim_{\substack{p \to 0 \\ \bar{v} \to \infty}} (p\bar{v}) = \bar{R}T$

Now, Avogadro gave a hypothesis after this. Now, pV is equal to m RT. We know after the Avogadro hypothesis was discovered, there is another way of expressing the mass of a substance. This is the m whose unit is kg in SI unit, but another way of expressing the amount of a substance as a fraction of its molecular weight. If I define n as a fraction of the molecular weight of the system; that means, not in terms of its actual mass in kg, but in terms of fraction.

For example, if there is 32 kg of oxygen. So, its n will be one, because the molecular weight of oxygen is 32. Similarly, 2 grams of hydrogen is one; that means, in that fraction 2 grams of hydrogen and 32 grams of oxygen are expressed in the same number, because these are the multiples of the molecular weight. If we express the mass in a different unit, what is that unit? Just scale it by the molecular weight 1 divided by M; multiply it by one by M. This unit is known as mole, number of mole. This is mass in kg, and if we do that and substitute these in the equation of state, we get n.

I am Sorry. Here we use R bar that we will be get. no Sorry no no no no no I am Sorry R all right. The R bar I will use in universal gas constant. If we substitute M is equal to n then M into R, I take in a bracket. So, this will be the modified equation of state when equation of state is expressed in terms of the number of moles of the substance. In equation of state, I do not want to use the mass, but I will use the mass in terms of the moles; that means, divided by molecular weight. So, M into R into nT. Now, Avogadro told that all gases at same pressure and temperatures with same number of moles have the same volume. If we have different gases whose number of moles is same that means their masses are proportional to their respective molecular weight. If they are at same pressure and temperature, they have equal volume which is not true for mass.

If we have got different gasses at different mass at same pressure and temperature, the volume will not be same. Density cannot be same, but if the number of moles is same for all gases at same pressure and temperature. They have the same volume. This is because of the same identity of the molecules; that means, molecules are alike.

This is the hypothesis which was given by Avogadro and because of this MR is same for all gases. Now MR, I write as R bar which is known as universal gas constant. Therefore, we see that if we replace M in terms of n, we can write pv is equal to n R bar T. R bar is nothing but molecular weight into R and which is a universal gas constant for all gases. These values, since it is universally constant for all gases should be remembered. This value is, we do not go more than two places of decimal, it will be enough to remember kilo Joule per kg mole Kelvin.

If I expect Something to be remembered, I should not go to an accuracy of four places of decimal which have been found out or theoretically or experimentally, it will be sufficient, because its unit will be Joule because this p into v is Joule in terms of kilo Joule per kg mole. R bar T, how do you find out kg mole that is kg by the molecular weight. This is the universal gas constant. If we write again, the two equations in terms of the specific volume, one is RT another is pv bar. I will use always these two equations. One is pv is equal to RT, small v is the specific volume, volume per unit mass. This is volume per unit mole, just one minute I will listen to all question.

It is volume per unit mole and R bar is the universal gas constant. So, the two equations are same; they are not independent equation. They are expressed in different form, where v is the specific volume. Here, v bar is the molar volume.

Okay please question

Excuse me sir

yes

(Refer Slide Time: 26:05) kg mole Kelvin. Do not use mole Kelvin wrong, that wrong you from now onwards you write kilo Joule per kg mole Kelvin. Usually some books write kg mole. Because kg mole has got a meaning that kg by molecular weight is the kg mole, gram by molecular weight gram mole. Do not use those nomenclatures given in some books like mole and kilo mole per kg mole, per gram mole. No kilo mole, it is kg mole, because mole has something to do with kg. So, mole molecular weight is dimensionless, So, kg by molecular weight is kg mole.

We can write kilo mole but I prefer it is kg mole or gram mole. This is my perception. I will better go with this.

One thing to be again remembered that for all real gases, limit of p into v bar as p tends to 0, or v bar tends to infinity, rarefied state becomes equal to R bar by T only as a limit, whereas an ideal gas will obey this, not as a limiting condition at all condition.

Next are two important corollaries of ideal gases. This is the definition of ideal gas starts with the equation of state.

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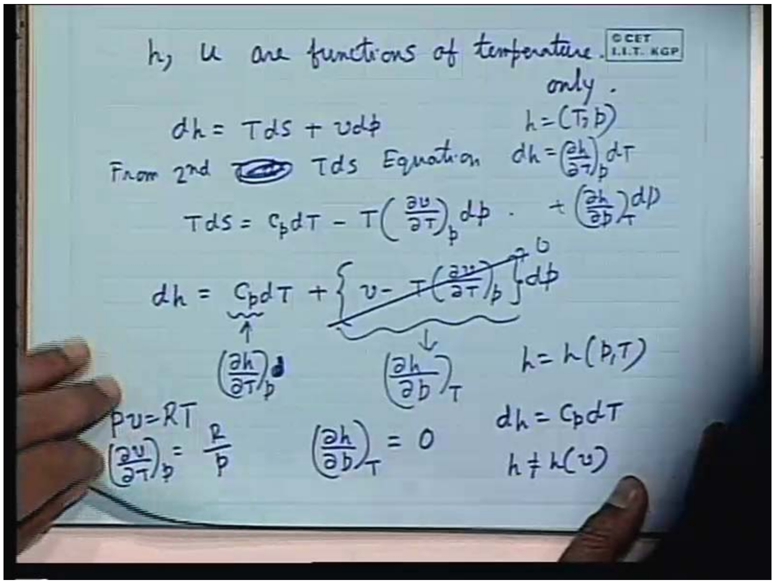

h, u are functions of temperature only.

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$dh = Tds + vdp$

$h = (T, p)$

From 2nd Tds Equation

$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$

$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$

$$dh = \underbrace{c_p dT}_{\left(\frac{\partial h}{\partial T}\right)_p} + \underbrace{\left\{ v - \overset{0}{\cancel{T\left(\frac{\partial v}{\partial T}\right)_p}} \right\}}_{\left(\frac{\partial h}{\partial p}\right)_T} dp$$

$h = h(p, T)$

$pv = RT$

$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$

$\left(\frac{\partial h}{\partial p}\right)_T = 0$

$dh = c_p dT$

$h \neq h(v)$

Now, two corollaries are that the specific enthalpy h or total enthalpy we can take. I will deal with specific values only and specific internal energy are functions of temperature. Here I tell you one thing. You will appreciate it afterwards just as an information, afterwards you will appreciate.

When the reaction part is not coming into picture, it is always better with the specific values rather than the molar values. But the molar properties come into picture when reactions are occurring; that means, when thermodynamics of the reactive systems come into picture. Because we will see, the significance of dealing with mole in case of reaction and the significance of dealing with mass, the specific property when reaction is not there. That is why, now, I will deal with the specific value. So, h and u are functions of temperature only. But probably you know by this time we have already derived it in course of our other studies but again I will do that.

How to prove that h and u are functions of temperature only? Let us write this expression that dh. If we recollect the very important thermodynamic property of relations which are most probably the most important and fundamental property relation is T ds plus v dp.

Now, what is Tds from the first Tds equation, second Tds equation? If we write from second Tds equation, we know that Tds, I am writing in terms of the specific entropy. Therefore, it will be cp dT minus T into del v this is the specific value v, c_p because s is specific at constant pressure dp. This is the second Tds equation. This is one of the very important relations Tds.

If we replace this, while finding out the Joule Kelvin coefficient; that is, the similar way, dh is equal to cp dT plus v minus T into del v divided by del T at constant p into dp. This c_p can be written as del h divided by del T at constant pressure that means h is a function of T and p that means as if dh is equal to, if I write h is a function of T and p, I can write del h divided by del T at constant pressure into dT plus del h divided by del p at constant temperature into dp. This we have already recognized.

This is nothing, but del h divided by del p at constant temperature. Now, what is this value for ideal gas? If we take the ideal gas equation, pv is equal to RT. If we use this to find this, this will be 0, because T del v divided by del T at constant p will be v.

If we differentiate del v divided by del T at constant pressure it is R by p. del v divided by del T at constant pressure will be R by p. RT by p means v, v minus v. Therefore, this becomes 0 which proves that del h divided by del p at constant temperature is equal to 0. Therefore, h becomes a function of temperature only. That means if I write dh is cp dT, from this equation, we can write dh is cp dT which means this h is a function of temperature only. h cannot become a function of any other quantity, because h can be expressed as p and T, but it is not a function. But how do we explicitly prove that h is not a function of volume that we can do? There are several ways.

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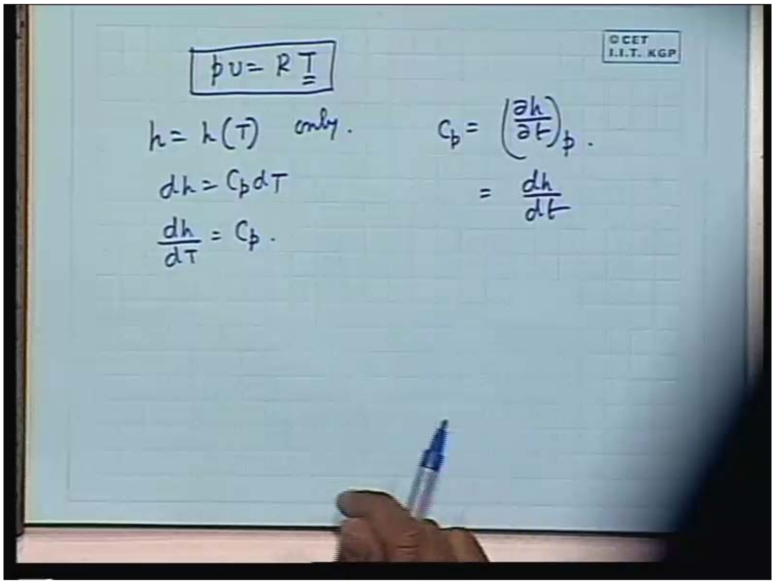

$$\boxed{pv = R\underline{\underline{T}}}$$

$h = h(T)$ only.

$dh = c_p dT$

$\frac{dh}{dT} = c_p$.

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p.$$

$$= \frac{dh}{dT}$$

One of the ways I am telling it is unnecessary that pv is equal to RT. So, if we keep the temperature fixed then volume will vary provided there is a variation in pressure. Therefore, at constant temperature, enthalpy cannot change with volume, if it does not change with pressure. Therefore, enthalpy does not change with volume, if it does not change with pressure at constant temperature, because this is the equation of state.

Therefore, we see enthalpy is a function of temperature only. The definition dh is equal to c_p dT which means dh divided by dT is equal to $c_{p.}$ Earlier, in first law, we recognized that definition of c_p is del h divided by del T especially, at constant pressure at p. This is valid for all substances. But since h is not the function of pressure, this can be simply written dh divided by dT. c_p is dh divided by dT. Similarly, we can show that u is also of function of temperature.

How to do it?

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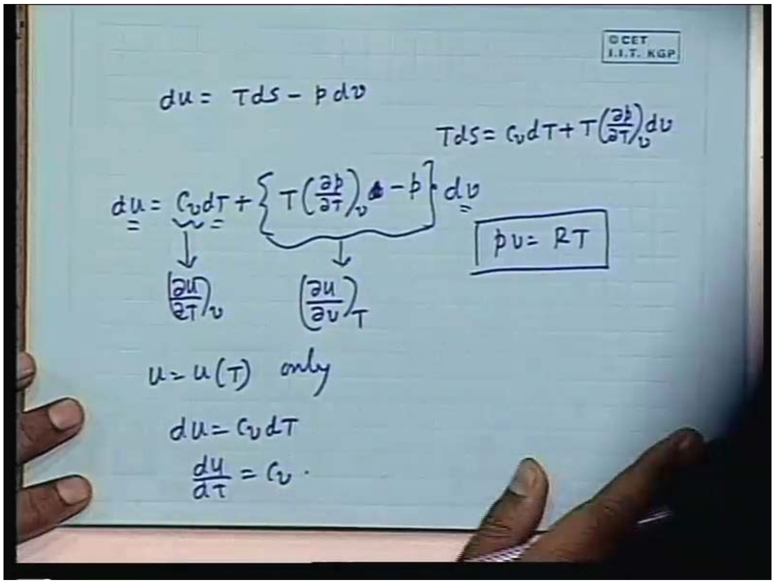

$$du = Tds - pdv$$

$$Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

$$du = \underbrace{c_v dT}_{\left(\frac{\partial u}{\partial T}\right)_v} + \underbrace{\left\{T\left(\frac{\partial p}{\partial T}\right)_v - p\right\}}_{\left(\frac{\partial u}{\partial v}\right)_T} dv$$

$$\boxed{pv = RT}$$

$u = u(T)$ only

$$du = c_v dT$$

$$\frac{du}{dT} = c_v .$$

In this case, we have to write du. We will start with du. What is this equation? Another fundamental and most important and popular expression is du minus pdv. Tds is du plus p dv. This is a probability relationship. Is it first law of thermodynamics?

yes sir

How many of you are telling yes.

du is equal to Tds minus p dv is the first law of thermodynamics

no no no no no

it is not the no it is not the first law of thermodynamics but can it be first law of thermodynamics

For a reversible process, with only displacement work, but this is the probability relationship. It may or may not be the first law of thermodynamics. It is first law of thermodynamics under a special situation. When the process is reversible and had only displacement work, as the work displacement mode of work as the work transfer du is equal to T ds minus p dv, because in the viva portion these questions will be asked. Nobody will ask you to deduce the Clausius-Clapeyron equations okay In a similar way, if we recall the first T ds equation. It is c_v dT plus T into del p divided by del T at constant v into dv.

We write it here, du is equal to c_v dT plus T into del p divided by del T at constant v minus p into dv. c_v is equal to del u divided by del T at constant ; that means, du is expressed as functions of T and p and this is nothing but del u divided by del v at constant T. What is this quantity?

If we evaluate this quantity for an ideal gas, where pv is equal to RT. This becomes 0; that means, u is a function of temperature only. These are very simple thing. Therefore, one of the important corollaries of the ideal gas is u and always du is equal to c_v dT. h and u are functions of temperatures.

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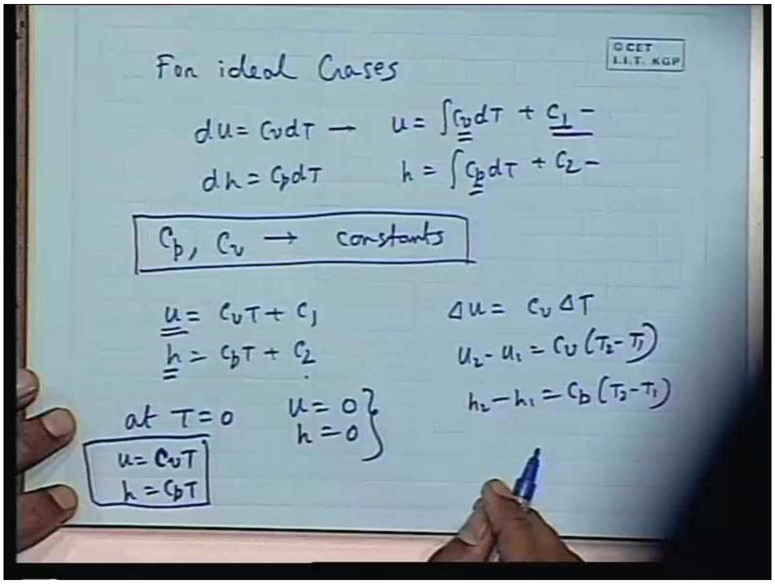

For ideal Gases

$du = C_v dT \rightarrow \quad u = \int \underline{\underline{C_v}} dT + \underline{\underline{C_1}} -$

$dh = C_p dT \qquad h = \int \underline{\underline{C_p}} dT + C_2 -$

$\boxed{C_p, C_v \rightarrow \text{constants}}$

$\underline{\underline{u}} = C_v T + C_1 \qquad \Delta u = C_v \Delta T$

$\underline{\underline{h}} = C_p T + C_2 \qquad u_2 - u_1 = C_v (T_2 - T_1)$

$h_2 - h_1 = C_p (T_2 - T_1)$

at $T = 0 \qquad \left.\begin{matrix} u = 0 \\ h = 0 \end{matrix}\right\}$

$\boxed{\begin{matrix} u = C_v T \\ h = C_p T \end{matrix}}$

Therefore, we come across this thing that for ideal gases, we can write du is equal to c_v dT and dh is equal to cp dT. If we make this is total internal energy then we make the heat capacity c_v, that both side multiply with much similar is the case. dH capital H that is the total enthalpy is the heat capacity c_p into dT.

If we integrate this, we will get u is equal to integration of c_v dT plus some arbitrary constant. Similarly, h is cp dT plus some arbitrary constant. These constants are neither functions of pressure nor function of volume, just simply a constant, numerical constant.

To express this u and h as a function of temperature, we have to integrate this equation. If we know this c_p and c_v explicitly as functions of temperature. For an ideal gas, we also assume c_p

and c_v are constants. They do not become the functions of temperature or any other properties. Sometimes, this is known as calorically ideal or calorically perfect gas. For ideal gas, when we tell, we always assume that it is a calorically ideal gas until and unless it is told. These are not very rigid things. Sometimes, we express that this is an ideal gas, but with a variation of c_p, c_v with temperature.

Sometimes, when we realize this assumption make this c_p, c_v varying with temperature, we tell the gas is semi ideal. So, several terminologies are there which has to be exclusively mentioned. If nothing is mentioned exclusively, if it is ideal gas given that means we will assume c_p, c_v are constants. But when c_p and c_v are constants, we tell that calorically perfect gas. Sometimes, perfect gas is a synonymous term for ideal gas.

If we consider a gas to be calorically perfect or ideal then c_p, c_v are constants. We consider for an ideal gas, another assumptions like pv is equal to RT as the equation of state that $c_{p,}c_v$ are constant. Then it becomes simply u is equal to c_v T plus c_1 is equal to c_p T plus $c_{2.}$ So, as long as the difference is considered, del u is equal to c_v into delta T. That means I can integrate this. If c_v is constant, then I do not care with this constant of integration. That means u_2 minus u_1 is equal to c_v T_2 minus T_1. This thing we have already used with the problems of first law h_2 minus h_1 is equal to c_p into T_2 minus T_1.

If I want to ascribe the specific internal energy, specific enthalpy at a particular state point, I have to know this c_1, $c_{2.}$ These c_1, c_2 are made by a convention for all ideal gases at T is equal to 0; both u is equal to 0, h is equal to 0 so that one can write u is equal to c_vT and h is equal to c_pT. So, these equations are valid.

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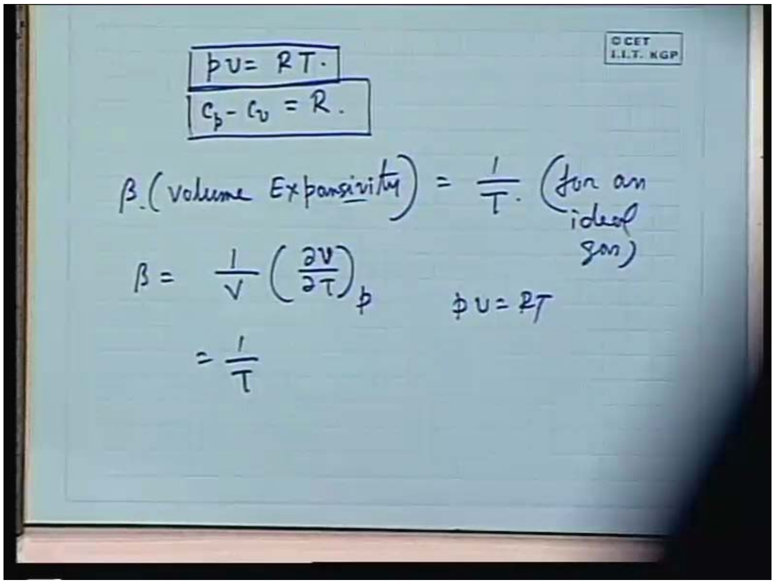

$$\boxed{pv = RT.}$$
$$\boxed{c_p - c_v = R.}$$

β (volume Expansivity) $= \frac{1}{T}.$ (for an ideal gas)

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad pv = RT$$
$$= \frac{1}{T}$$

Already we have proved another result that if pv is equal to RT is the equation of state, v is the specific volume. Then the value of cp minus cv is R. This already we have proved from thermodynamic relation; c_p and c_v. From two tedious equations, we found out the expression of cp minus cv in terms of the derivative of other thermodynamic properties and utilize this relationship as the equation of state for ideal gas. We have shown that cp minus cv is equal to R. This is one of the important relations for an ideal gas.

Another important relationship for ideal gas which is often used in heat transfers studies. That beta, which I defined earlier, is the volume expansibility or volume expansion coefficient. When we read heat transfer then beta for an ideal gas is 1 by T then, you will not be able to tell them your heat transfer teacher may ask that how you have read thermodynamics.

It may not be very much related to thermodynamic studies in free convection studies on heat transfer. We always encounter with this parameter v; volume expansibility is 1 by T for ideal gases. Do not consider that this definition is 1 by T for an ideal gas. I will now prove by simple two line proof. Beta definition is 1 by v del v divided by del T at constant pressure.

We use pv is equal to RT and get these things 1 by T pv is equal to RT. Find out del V divided by del T from here at constant pressure and get these things. We will get simply 1 by T volume expansibility. We see the dimension is temperature, and it exactly becomes 1 by the absolute temperature in case of an ideal gas.

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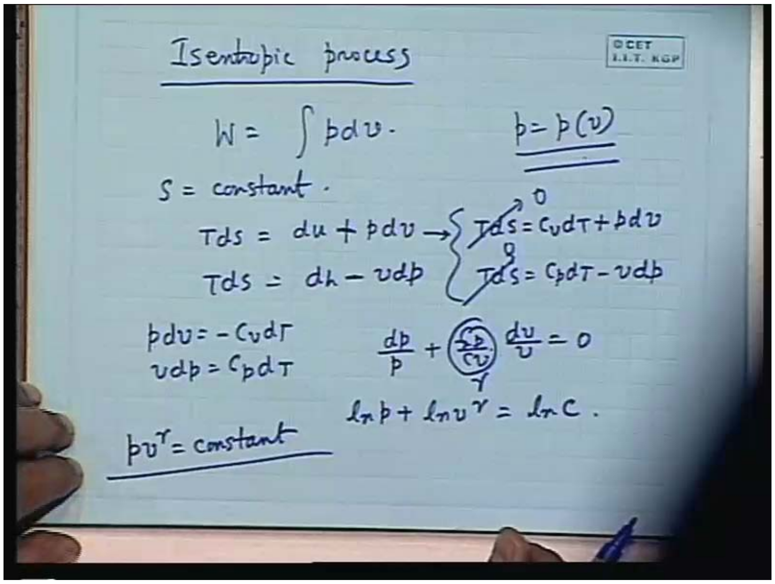

Isentropic process

$$W = \int p\,dv. \qquad p = p(v)$$

s = constant.

$$T\,ds = du + p\,dv \rightarrow \overset{0}{\cancel{T\,ds}} = C_v\,dT + p\,dv$$

$$T\,ds = dh - v\,dp \qquad \overset{0}{\cancel{T\,ds}} = C_p\,dT - v\,dp$$

$$p\,dv = -C_v\,dT$$

$$v\,dp = C_p\,dT$$

$$\frac{dp}{p} + \underbrace{\boxed{\frac{C_p}{C_v}}}_{\gamma}\frac{dv}{v} = 0$$

$$\ln p + \ln v^{\gamma} = \ln C.$$

$$pv^{\gamma} = \text{constant}$$

Another very important relations for pv for a particular process in an isentropic process. We know that displacement work W is integral of p dv per unit mass. But can we integrate this? To integrate this, we have to know p as a function of volume. Therefore, we have to know the path along which the process has executed this work transfer. That path is specified by the functional relationship of pv that depends upon path to path. So, if we know this relationship, we can integrate this. One of the paths is isentropic process.

Let us consider that isentropic process. s is equal to constant. Basically, isentropic process is a reversible adiabatic process. Now, we write very two important equations; T ds is du minus pdv and T ds is dh minus vdp. For ideal gas, this equation is valid for all processes property relationship.

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yes

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First one is Tds is du plus second one negative. These two equations are property relations valid for all. Now, if I write this as T ds is equal to c_v dT plus pdv. Is it valid for all systems?

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It is valid for ideal gas.

A form of this equation only for ideal gases and this is also cp dT minus vdp. It is valid for ideal gases. Now, I will write these two property relations for ideal gases and consider an isentropic process that means the left hand side is 0. Then if we divide one by other that means if we take this side that means pdv is equal to c_v dT and vdp minus and vdp is cp dT. We divide it then we get dp by p plus cp by cv into dv. I know the result. So without seeing that I am writing you can also write it it will come like this.

If this is represented as gamma and integrates it; that is, ln p plus ln v gamma, gamma lnv means lnv to the power gamma and in that case, constant is also logarithm of some constant ln c. So, that pv gamma is constant. This is a very important relationship for an isentropic process. In school probably, you have done this.

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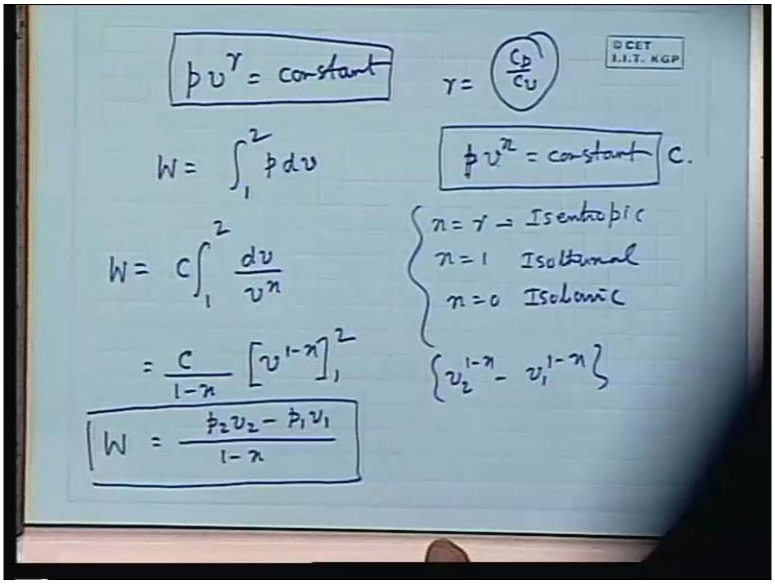

$$\boxed{pv^{\gamma} = \text{constant}} \qquad \gamma = \frac{c_p}{c_v}$$

$$W = \int_1^2 p\,dv \qquad \boxed{pv^{n} = \text{constant}}\ c.$$

$$W = c\int_1^2 \frac{dv}{v^n}$$

$$\left\{\begin{array}{l} n = \gamma \rightarrow \text{Isentropic} \\ n = 1 \quad \text{Isothermal} \\ n = 0 \quad \text{Isobaric} \end{array}\right.$$

$$= \frac{c}{1-n}\left[v^{1-n}\right]_1^2 \qquad \left\{v_2^{1-n} - v_1^{1-n}\right\}$$

$$\boxed{W = \frac{p_2v_2 - p_1v_1}{1-n}}$$

pv gamma is constant is valid for an isentropic process executed by an ideal gas, where gamma is constant and equals to cp by cv. Gamma is always greater than one, because c_p is always greater than c_v that has been already proved.

Now if I equate this is one important thing, we can think it trivial it is not very important but one you do it. It is better that remember this formula otherwise there will be no problem in deriving this.

If we have to evaluate this integral from a point one to state point two, and if we have got a relationship of this Sometimes for all other processes, so all other reversible processes, it is possible to express the relationship as this pv n is equal to constant, where n has got any value. When n is equal to gamma the process is isentropic. When n is equal to 1, the process is isothermal. pv isothermal for an ideal gas, all for ideal gas and n is equal to 0 isobaric.

For any value of n which may not be equal to1, gamma, 0? It represents the reversible process which may not be isentropic, may not be constant pressure, may not be constant temperature, but it is a reversible process. When a reversible path of the process is prescribed by a functional relationship of pv in the form of a power law that p v to the power n is constant. Then one can integrate this. Let this is equal to constant c. Then one can relate it constant, dv divided by v n. So, if we do this, then we get v c 1 minus n from one to two. So, two v_2 one minus n and c is p_2 v_2 n. So, this becomes p_2 v_2 minus p_1 v_1 by 1 minus n, because v_2 one minus n minus v_1 this bracket. After putting the limit, this will be like that.

When it will be multiplied with c which is p_2 v_2 n, here that is p_2 $v_{2,}$ when we will multiply with that we will use p_1 $v_{1.}$ So, this is a very important expression. If n is equal to gamma, this will be one minus gamma. So, depending upon the value of the index and the corresponding values of pv is that initial and final state, the sign of W will be determined so that we can find out whether the work is coming out or work is going into the system. Next is pdv for a polytrophic process. Then we come to the entropy change of an ideal gas.

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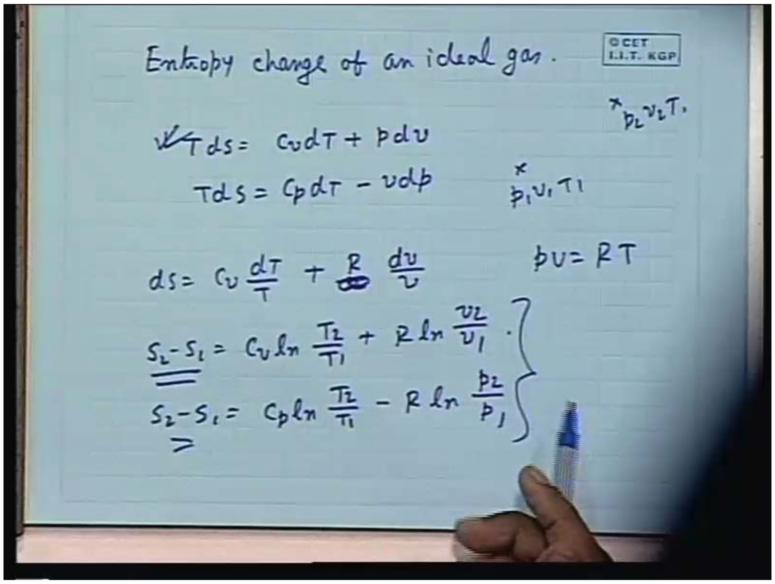

Entropy change of an ideal gas.

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$$T\,ds = c_v dT + p\,dv$$

$$T\,ds = c_p dT - v\,dp$$

$\times\ p_2 v_2 T_2$

$\times\ p_1 v_1 T_1$

$pv = RT$

$$ds = c_v \frac{dT}{T} + \frac{R}{\cancel{}} \frac{dv}{v}$$

$$\left.\begin{aligned} \underline{\underline{s_2 - s_1}} &= c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}. \\ s_2 - s_1 &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1} \end{aligned}\right\}$$

How to calculate the entropy change of an ideal gas? The entropy change of an ideal gas is very simple. Again we start from the same equation that T ds is equal to c_v dt plus pdv, T ds is equal to cp dT minus vdp.

Now, for the two points, pressure, volume, and temperature, all these things may not be given. We may know pressure temperature, we may know volume temperature or we know everything. So, we can use any pair. So, if we use the temperature and volume, we use this ds is equal to c_v dT by T. pv is equal to RT. So, p by T is equal to R dv by v. Therefore, s_2 minus s_1 is c_v ln T_2 by T_1 plus R ln v_2 by v_1. Any question all right it is very simple school level.

Similarly, we integrate the second one. We get c_p ln T_2 by T_1 minus R ln p_2 by p_1. So, the change in entropy between these two states given by T and v and p and T we can use, and p and v we can make from these two equations. We can find out the relationship between p and v. This way we can find out the expression for entropy change of an ideal gas. Therefore, we have to remember for ideal gas all those corollaries while solving problems.

After this I will start the real gas, what is a real gas? The few real gases and how we can express the equation of state for a real gas.

But I think today the time is limited the time much time is not there. So, I will start the expressions for real gas. How it deviates from the ideal gas and how we can express the equation of state of a real gas compressibility factor and all these things. I will discuss in the next class.

But before that you ask me any questions you do have. Today is extremely simple what I have taught. But regarding just a minute till five minutes we can spare if you feel So that we can discuss anything about the change of phase diagram and all. Any questions? No question.