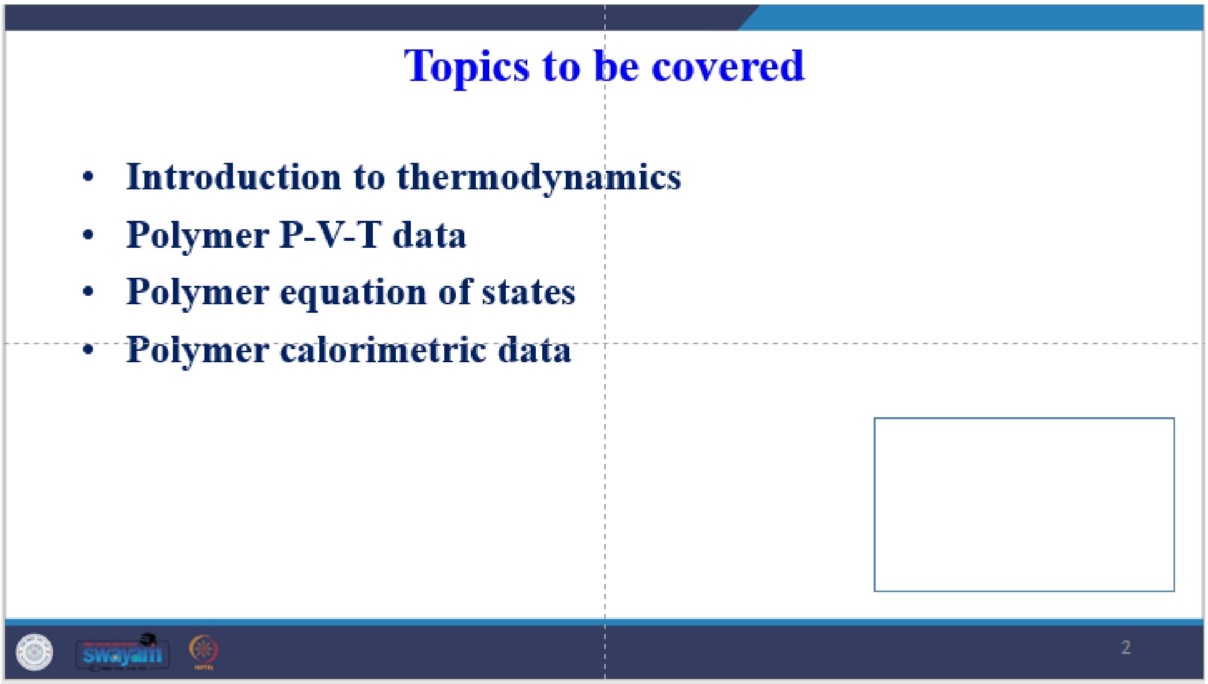
Polymer Process Engineering

Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture – 06

Thermodynamics of polymer systems-I

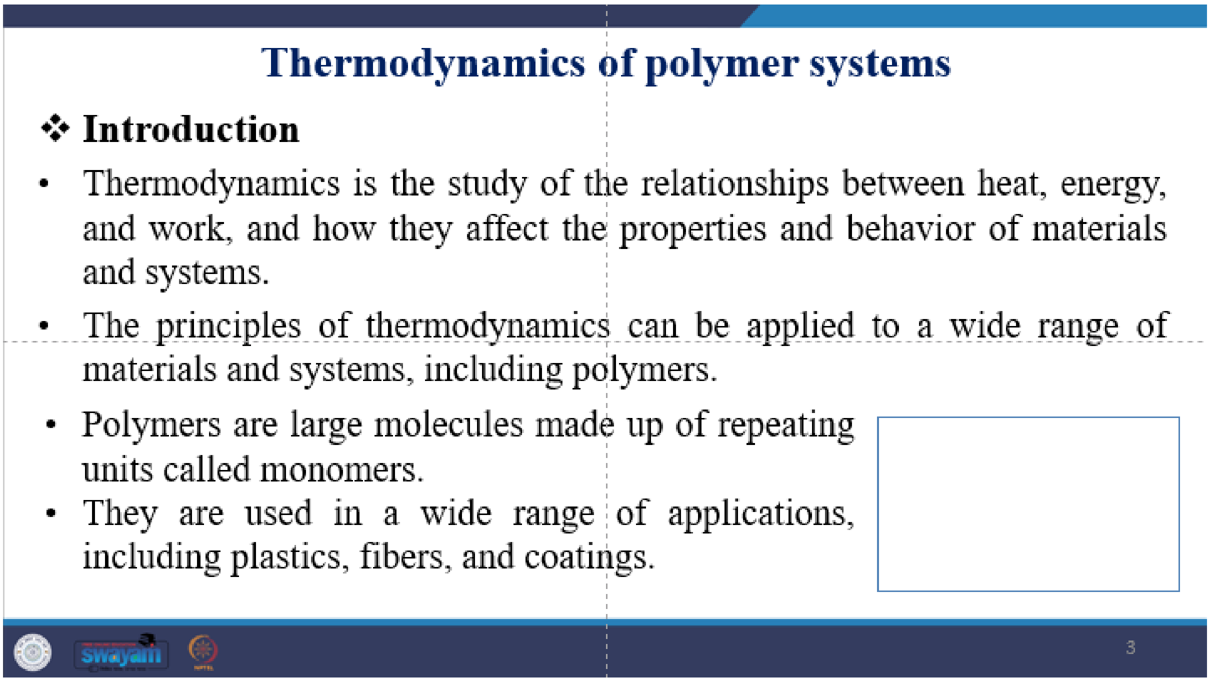
Hello friends, welcome to the thermodynamic aspect of polymeric system. Now thermodynamics play a very vital role because sometimes the heat of reaction, sometimes other exothermicity or endothermicity plays a very vital role in the polymeric system or polymeric reaction mass. So, the knowledge of all these things and you can say this is the backbone of your polymerization process and a polymer system. So, the awareness about the thermodynamic character of the polymeric system is extremely important. So, by this way we are starting this thermodynamic aspect of the polymeric system under the edges of polymer process engineering. So, let us take up with the first segment of this thermodynamics aspect.



Topics to be covered

- Introduction to thermodynamics
- Polymer P-V-T data
- Polymer equation of states
- Polymer calorimetric data

Now in this particular segment we are going to cover what is the thermodynamics, then we will discuss about the polymeric PVT data, then we will discuss about the equations pertaining to the equation of state, especially with respect to the polymer system, then we will discuss about the polymer calorimetric data. Now the thermodynamics usually is the study of the relationship between the heat, energy and work or among the heat, energy and work and how they affect the various properties of any system, chemical species or polymeric system. In principle, the thermodynamics which can be applied to the wide range of the materials system this including the polymer. Now this is the polymers are the large molecules made up of a repeating unit, they are called the monomer.



Thermodynamics of polymer systems

❖ Introduction

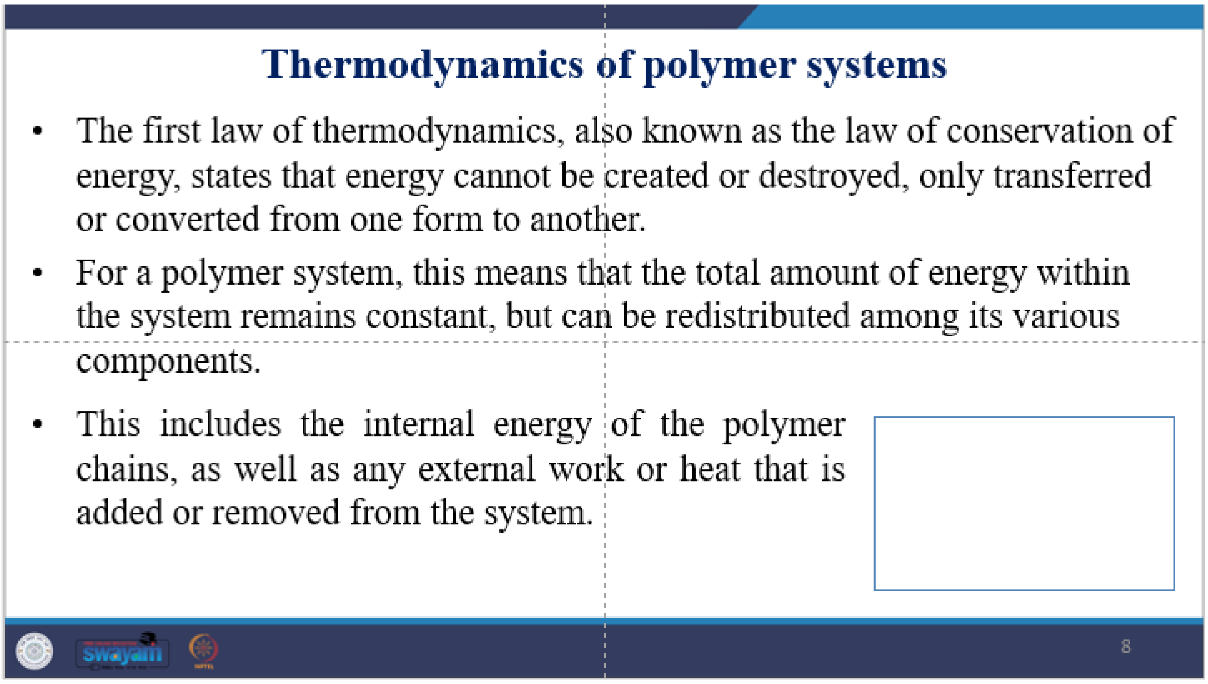
- Thermodynamics is the study of the relationships between heat, energy, and work, and how they affect the properties and behavior of materials and systems.
- The principles of thermodynamics can be applied to a wide range of materials and systems, including polymers.
- Polymers are large molecules made up of repeating units called monomers.
- They are used in a wide range of applications, including plastics, fibers, and coatings.

So, they are used in a wide range of application right from day to day affair to the specialized thing. Now, the thermodynamics of polymeric system is usually concerned with the understanding behaviour of the polymer in different conditions, different conditions pertaining to the pressure, temperature, chemical exposure, atmospheric exposure, environmental attack, all these things. So, the thermodynamic property, the knowledge of the thermodynamic property is quite essential. The thermodynamic properties of polymers they are influenced by the molecular structure of the polymer and the degree of polymerization and the chemical composition of the monomer. Now these properties can be studied by using various techniques like instrumental techniques like differential scanning calorimetry or thermal gravimetric analysis.

Now usually these techniques measure the thermal behaviour of the polymers or weight loss of the polymers and usually they are represented as a function of temperature. The thermodynamic of the polymeric system, this also plays a critical role in understanding the behaviour of the polymers in various industrial and engineering application. Let us take an example, the thermodynamic principle can be used to predict the stability and the shelf life of polymer in different environment. Like if you are using any chair from 0 degree Celsius to say 47-degree Celsius atmospheric temperature, then how you can predict the shelf life of a polymer up to how long it goes in a workable situation. This can be the thermodynamic data is useful in predicting this kind of life cycle analysis.

Now to design the polymer with specific properties because sometimes you have the granules and you need to convert all these granules into useful products like chairs or any commodity item. Then you require the heat and energy in that particular aspect the knowledge about the thermodynamic principle is quite essential, and to optimize the processing condition of the polymer production, the thermodynamic data gives useful information. Suppose any polymer melts at say 60 degrees Celsius, so you cannot go beyond 100 degrees Celsius otherwise, it may tend to have different properties it may get charged. So, all kinds of thermodynamic data are quite essential the knowledge of all these data is quite essential. So, the overall study of the thermodynamics of polymer systems is important for understanding the fundamental properties and the behaviour of the polymers as well as developing new materials and applications that can benefit from a unique property of the polymer.

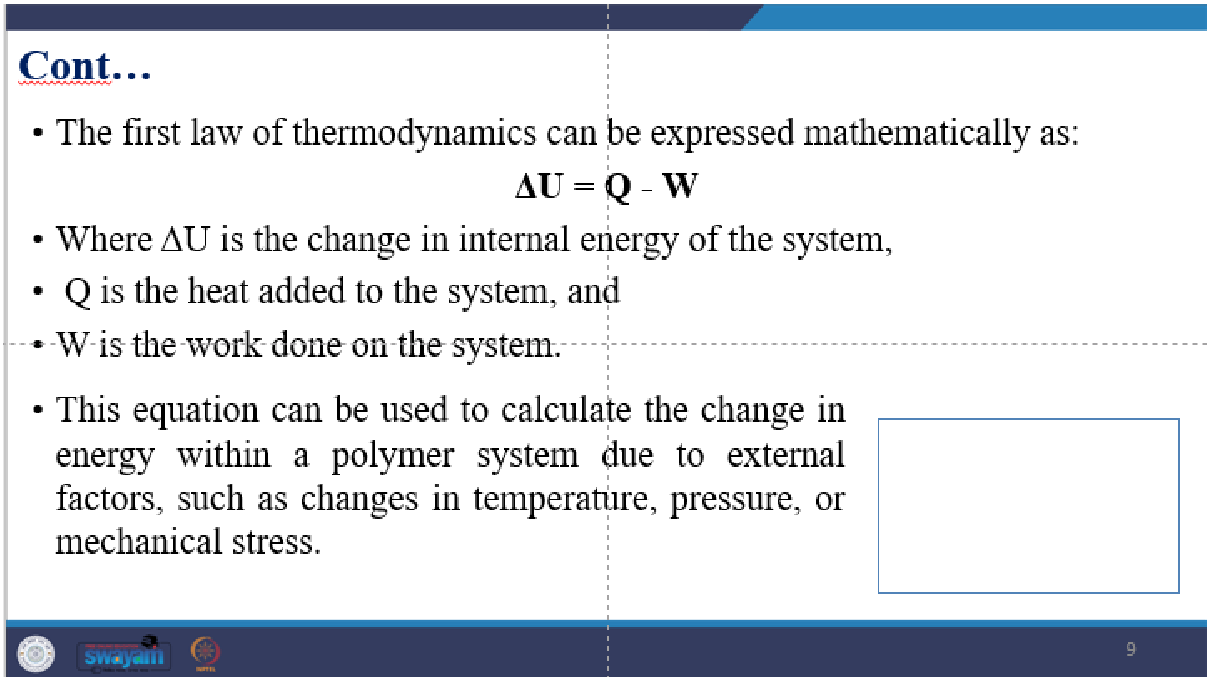
Now usually thermodynamics is governed by the various laws and in practice there are four laws zeroth law, first law, second law, third law. So, these laws they supplement to various thermodynamic principle and based on these principles and laws a various kind of thermodynamic equations being derived. One of the important laws is the first law, so the first law of thermodynamics which is known as the law of conservation of energy states that energy cannot be created or destroyed only transferred or converted from one form to another form. For a polymeric system this means the total amount of energy within the system remains constant but can be redistributed among its various components. Now this includes the internal energy of the polymer chain as well as any external work or heat is then added or removed from the system.



Thermodynamics of polymer systems

- The first law of thermodynamics, also known as the law of conservation of energy, states that energy cannot be created or destroyed, only transferred or converted from one form to another.
- For a polymer system, this means that the total amount of energy within the system remains constant, but can be redistributed among its various components.
- This includes the internal energy of the polymer chains, as well as any external work or heat that is added or removed from the system.

So, the first law of thermodynamics this can be expressed mathematically that is delta u is equal to q minus w, delta u is the change in the internal energy of the system. So, if you supply any or it can be modified like this q is equal to delta u plus w. So, if you supply the q amount of heat to the system then certain quantity of the heat can be consumed to raise or to alter the internal energy of the system and remaining you can utilize as a work. So, w is the work done into the system and delta u is the change in the internal energy of the system. So, this equation can be used to calculate the change in energy within a polymeric system due to the external factors like change in the temperature, pressure or mechanical stress.



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- The first law of thermodynamics can be expressed mathematically as:

$$\Delta U = Q - W$$

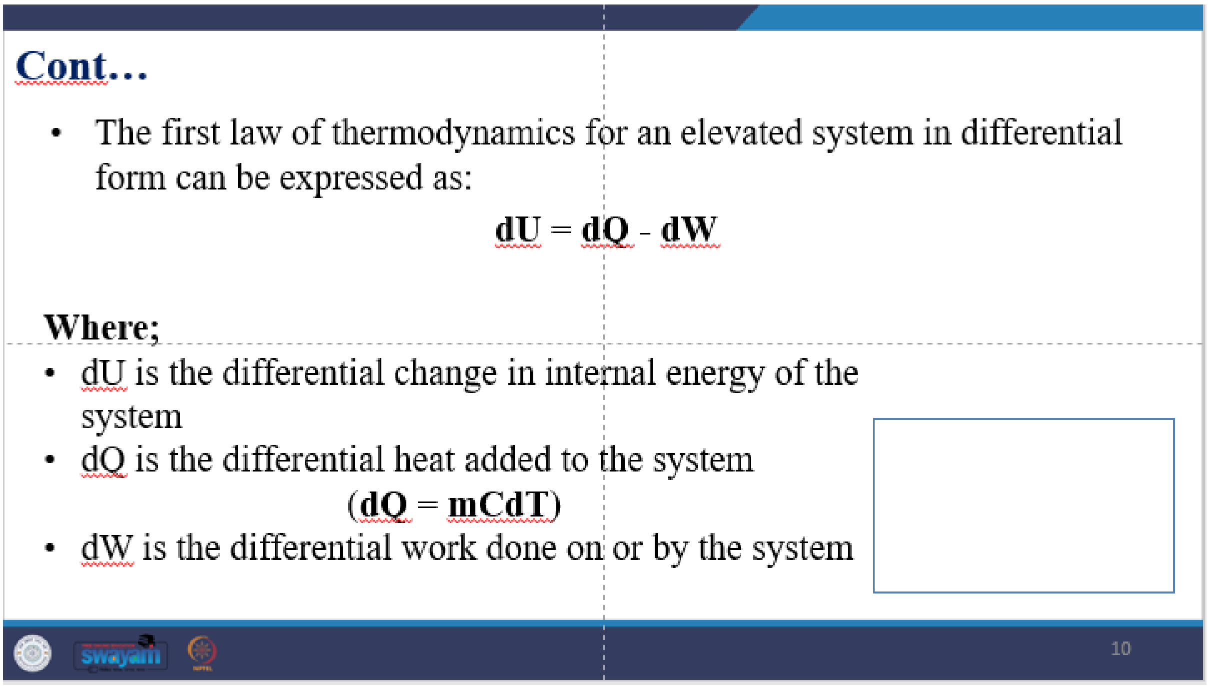
- Where ΔU is the change in internal energy of the system,
- Q is the heat added to the system, and
- W is the work done on the system.
- This equation can be used to calculate the change in energy within a polymer system due to external factors, such as changes in temperature, pressure, or mechanical stress.

So, in the differential form this thermodynamic law can be represented as dU is equal to dQ minus dW, dU is the differential change in the internal energy, dQ is the differential heat added to the system and dW is the differential work done by the system. So, sometimes in thermodynamic system this the dQ is represented as dQ is equal to m c delta t. So, dW or work this can be represented as dW is equal to fdh where f is the force being applied or acting to the system and d h is the differential change in the distance or height whatever you can say. So, if we substitute this particular these things into the differential form of the first law of thermodynamics which we represented over here we can get the modified equation of dU is equal to mCdelta t minus fdh. This equation describes the differential change in the internal energy of an elevated system due to the differential change in temperature and height.

$$dU = dQ - dW$$

$$(dQ = mCdT)$$

$$dU = m\,C\,dT - F\,dh$$



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- The first law of thermodynamics for an elevated system in differential form can be expressed as:

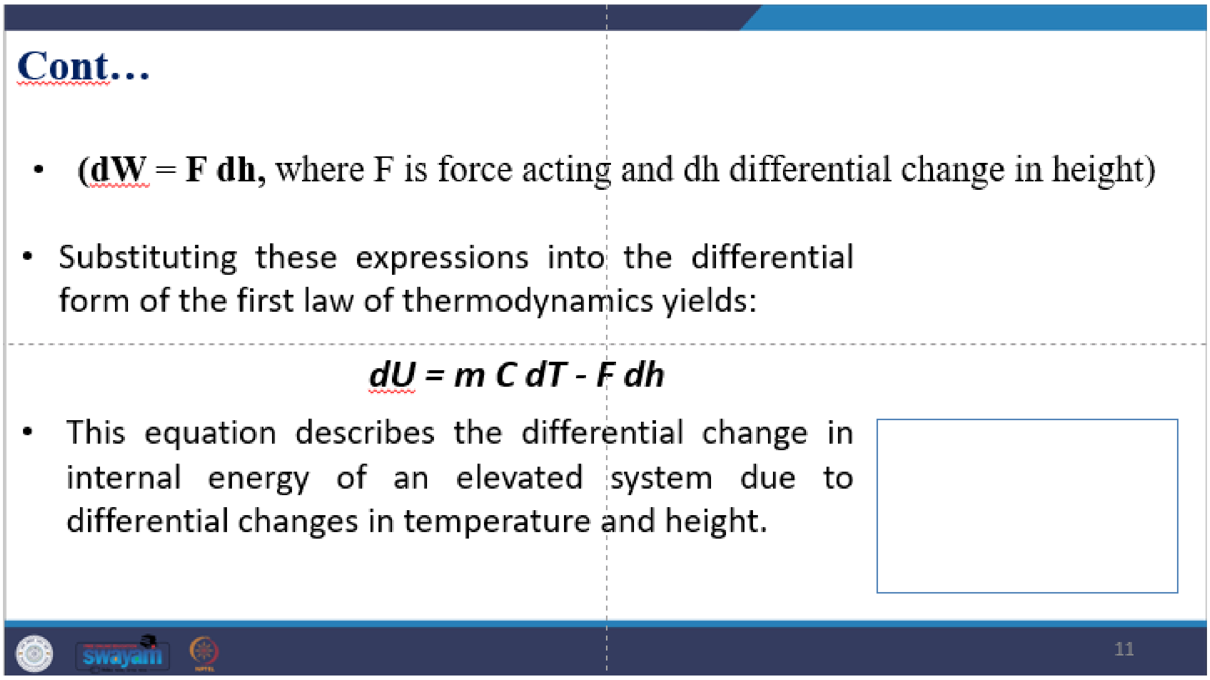
$$dU = dQ - dW$$

Where;

- dU is the differential change in internal energy of the system
- dQ is the differential heat added to the system

$$(dQ = mCdT)$$

- dW is the differential work done on or by the system



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- (**dW = F dh,** where F is force acting and dh differential change in height)
- Substituting these expressions into the differential form of the first law of thermodynamics yields:

$$dU = m\,C\,dT - F\,dh$$

- This equation describes the differential change in internal energy of an elevated system due to differential changes in temperature and height.

Another thing is very important that is enthalpy because when we heat the system then we must know about the thermal behavior or response towards the thermal behavior of any polymeric system. So, the enthalpy is a useful tool to get this kind of information. So, this can be defined for a system involving the expansion of work p v because sometimes polymer is composed of the chains. So, if you heat then definitely the chains are unentangled to give some sort of expansion work. So, this can be defined this can be very good predicted by the enthalpy.

So, the enthalpy mathematically can be represented as H is equal to U plus PV this is the very generic equation V is the specific volume U is the internal energy, and P is the pressure. Now, Cp sometimes the change in the specific heat at constant temperature is again very useful which is has the unit of joule per kilogram Kelvin. Now Cp is equal to dh over dt at constant pressure. This is again very useful tool. Therefore, the enthalpy for constant pressure system can be represented as dH is equal to Cp dt the specific heat associated with the constant volume is defined at Cv is equal to delta U over delta T at one at constant volume, and then Cp minus Cv is again very useful thing this can be given as T epsilon square over rho theta.

$$H = U + PV$$

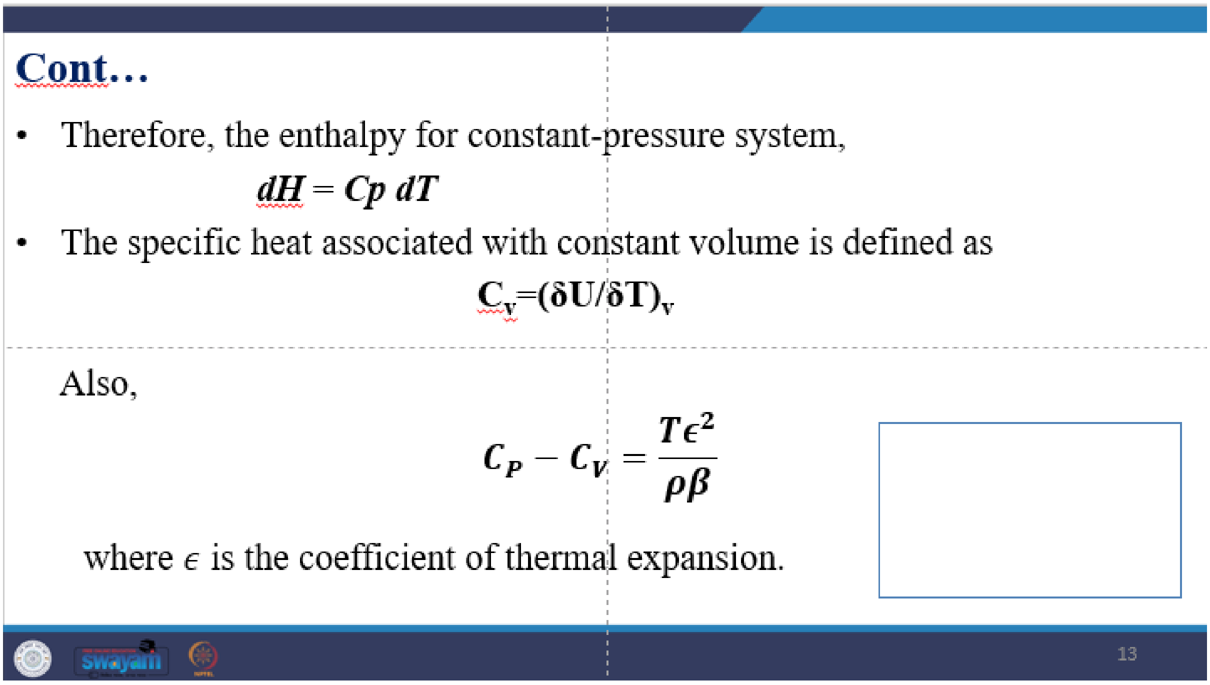
$$C_P = (\delta H/\delta T)_P$$

$$dH = C_p\, dT$$

$$C_V = (\delta U/\delta T)_V$$

$$C_P - C_V = \frac{T\epsilon^2}{\rho\beta}$$

Now epsilon is the coefficient of thermal expansion. Now it is quite evident that whenever you are heating any polymer then there may be certain expansion with attributed to the chains and all those things. So, you need to have this particular information handy. Now the coefficient of thermal expansion can be given as epsilon is equal to minus 1 upon rho del over rho del rho over del T at constant P this can be given as 1 over V into del V over del T at constant P. Now in the previous equation we use this beta this is the coefficient of compressibility factor.



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- Therefore, the enthalpy for constant-pressure system,

$$dH = Cp\ dT$$

- The specific heat associated with constant volume is defined as

$$C_V = (\delta U/\delta T)_V$$

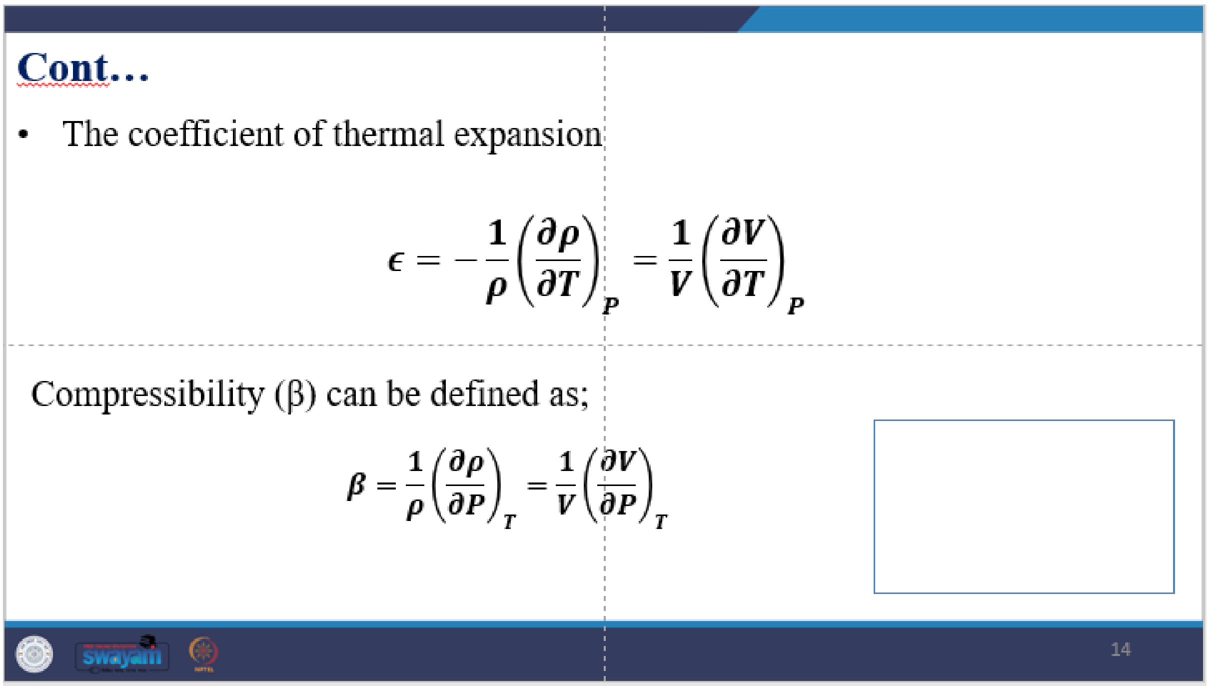
Also,

$$C_P - C_V = \frac{T\epsilon^2}{\rho\beta}$$

where ϵ is the coefficient of thermal expansion.

$$\epsilon = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\beta = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$



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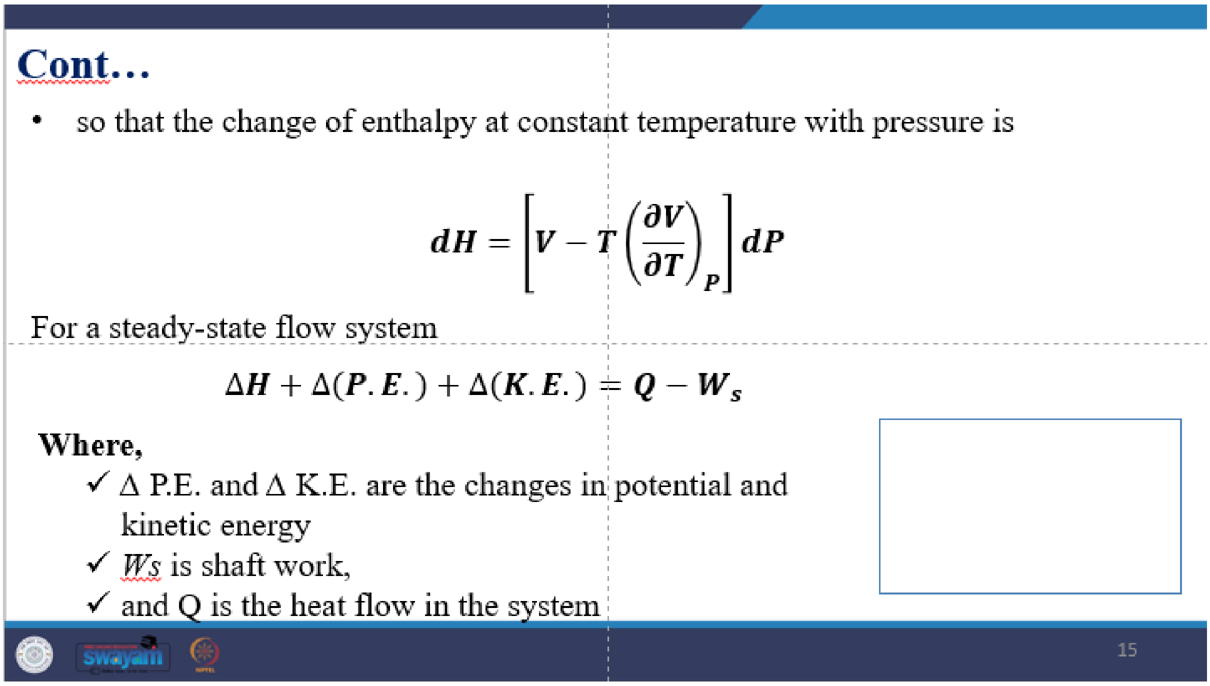
- The coefficient of thermal expansion

$$\epsilon = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Compressibility (β) can be defined as;

$$\beta = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

So, compressibility beta can be defined as beta is equal to 1 Over rho del rho over del P at constant t. Which is equal to 1 over del V over del P at constant T. So, the change in the enthalpy at constant temperature with pressure is given as dH is equal to V minus T del V over del T at constant P into dP. For a steady flow system, it can be represented as delta H is delta H plus change in the potential energy plus change in kinetic energy that is equal to Q minus Ws where Ws is the shaft work and these are the potential energy and kinetic energy and Q is the heat flow in the system. Now the second law of thermodynamics again it is impossible to convert a given quantity of heat completely into work. So, the property associated with the second law is mainly the entropy, which is usually represented as S.



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- so that the change of enthalpy at constant temperature with pressure is

$$dH = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

For a steady-state flow system

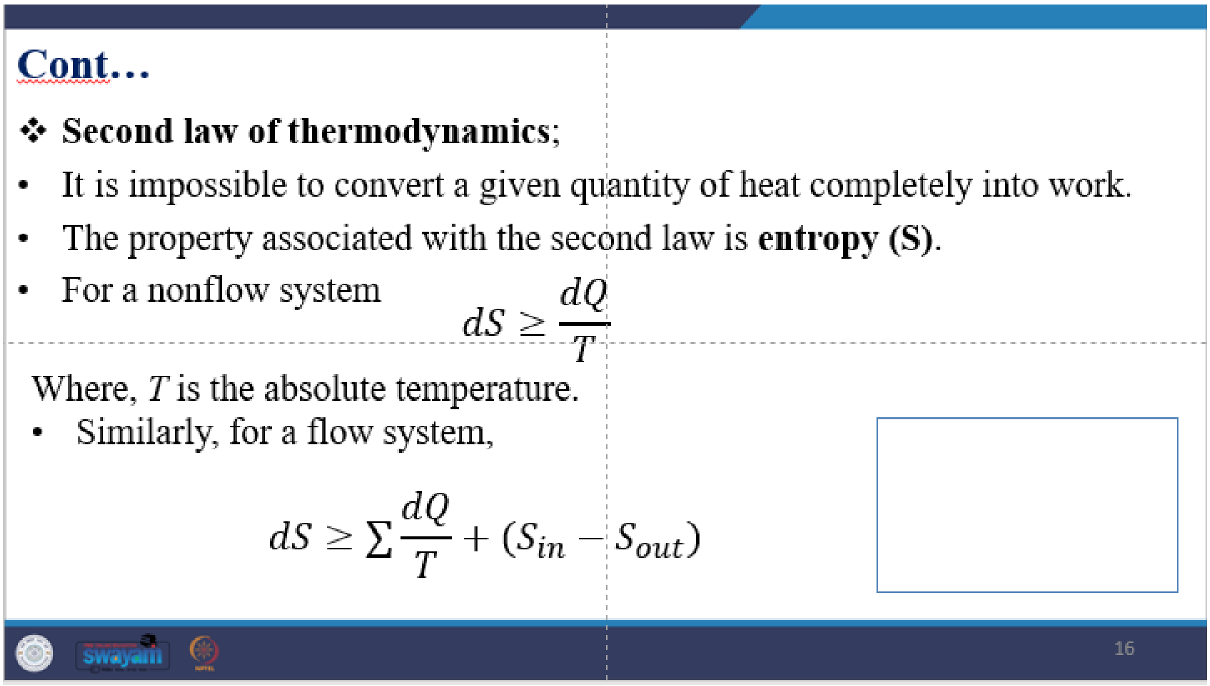
$$\Delta H + \Delta(P.E.) + \Delta(K.E.) = Q - W_s$$

Where,

- ✓ Δ P.E. and Δ K.E. are the changes in potential and kinetic energy
- ✓ *Ws* is shaft work,
- ✓ and Q is the heat flow in the system

$$\boldsymbol{dH = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP}$$

$$\Delta \boldsymbol{H} + \Delta(\boldsymbol{P.E.}) + \Delta(\boldsymbol{K.E.}) = \boldsymbol{Q} - \boldsymbol{W_s}$$



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- **Second law of thermodynamics;**
- It is impossible to convert a given quantity of heat completely into work.
- The property associated with the second law is **entropy (S)**.
- For a nonflow system $dS \geq \frac{dQ}{T}$

Where, T is the absolute temperature.

- Similarly, for a flow system,

$$dS \geq \sum \frac{dQ}{T} + (S_{in} - S_{out})$$

$$dS \geq \frac{dQ}{T}$$

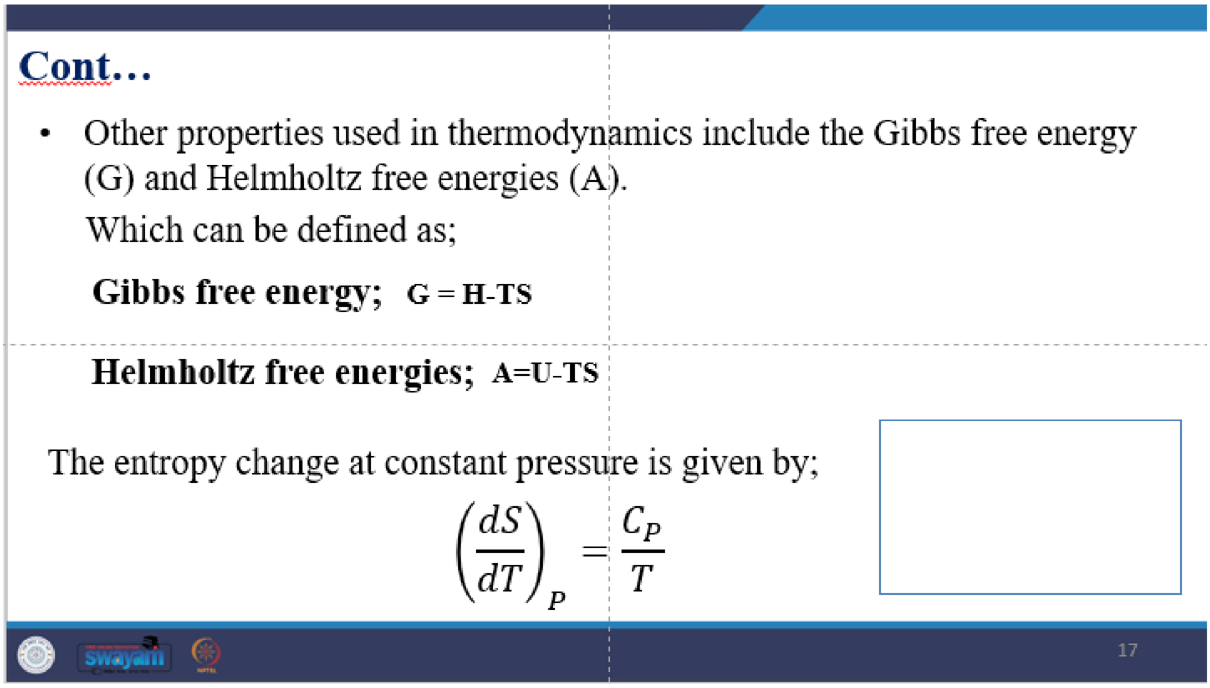
$$dS \geq \sum \frac{dQ}{T} + (S_{in} - S_{out})$$

So, for non-flow system, it can be dS, which is greater than equal to dQ over T where T is the absolute temperature. Now similarly if we talk about the flow type of a system, then dS are greater than or equal to summation dQ over T plus Sin and out. So, the other properties, when we talk about the other properties in the thermodynamics this includes the Gibbs free energy and Helmholtz free energy or Helmholtz work function which can be defined as the Gibbs free energy. This is represented as G, H is enthalpy T is temperature, S is entropy and Helmholtz work function Helmholtz free energy this can be given as A is equal to U minus TS, U is the internal energy. So, the entropy changes at constant pressure this can be given as dS over dT at constant pressure that is given as Cp over T this is a general thermodynamic equation and the change in the entropy at constant pressure This can be defined as dS is equal to Cp over T dT.

Gibbs free energy; G = H-TS

Helmholtz free energies; A=U-TS

$$\left(\frac{dS}{dT}\right)_P = \frac{C_P}{T}$$



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- Other properties used in thermodynamics include the Gibbs free energy (G) and Helmholtz free energies (A).

  Which can be defined as;

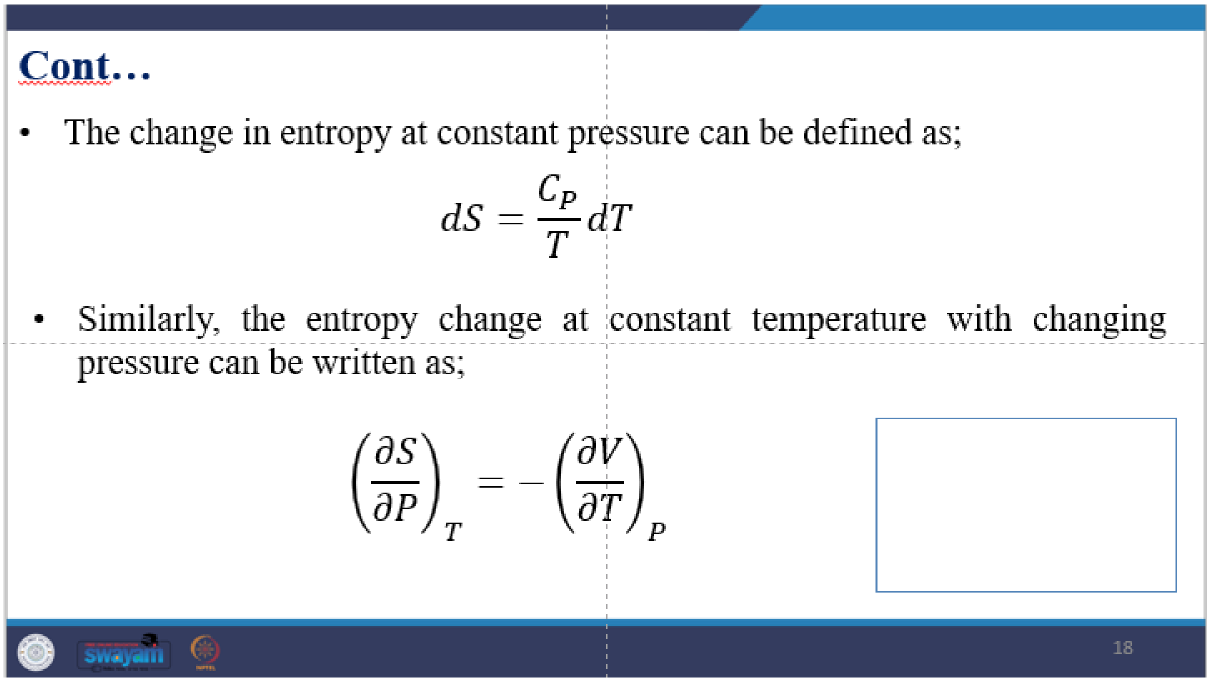
  Gibbs free energy; **G = H-TS**

  Helmholtz free energies; **A=U-TS**

The entropy change at constant pressure is given by;

$$\left(\frac{dS}{dT}\right)_P = \frac{C_P}{T}$$

Now similarly, the entropy change at constant temperature with changing pressure this can be written as del S over del P at constant temperature that is minus del V over del T at constant pressure. This is sometimes referred as the Maxwellian equations. Therefore, the change in entropy in the differential form which we can represent as dS is equal to minus del V over del T at constant P d P. So, let us talk about the polymer pressure volume temperature data. Now see the pressure volume temperature the PVT data they are very important the reason is that if we need to define any kind of thermodynamic system or especially any kind of a system with respect to the thermodynamics there are 8 different parameters needed and out of 8 this can be the pressure volume temperature are only 3 parameters which you can measure directly.



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- The change in entropy at constant pressure can be defined as;

$$dS = \frac{C_P}{T} dT$$

- Similarly, the entropy change at constant temperature with changing pressure can be written as;

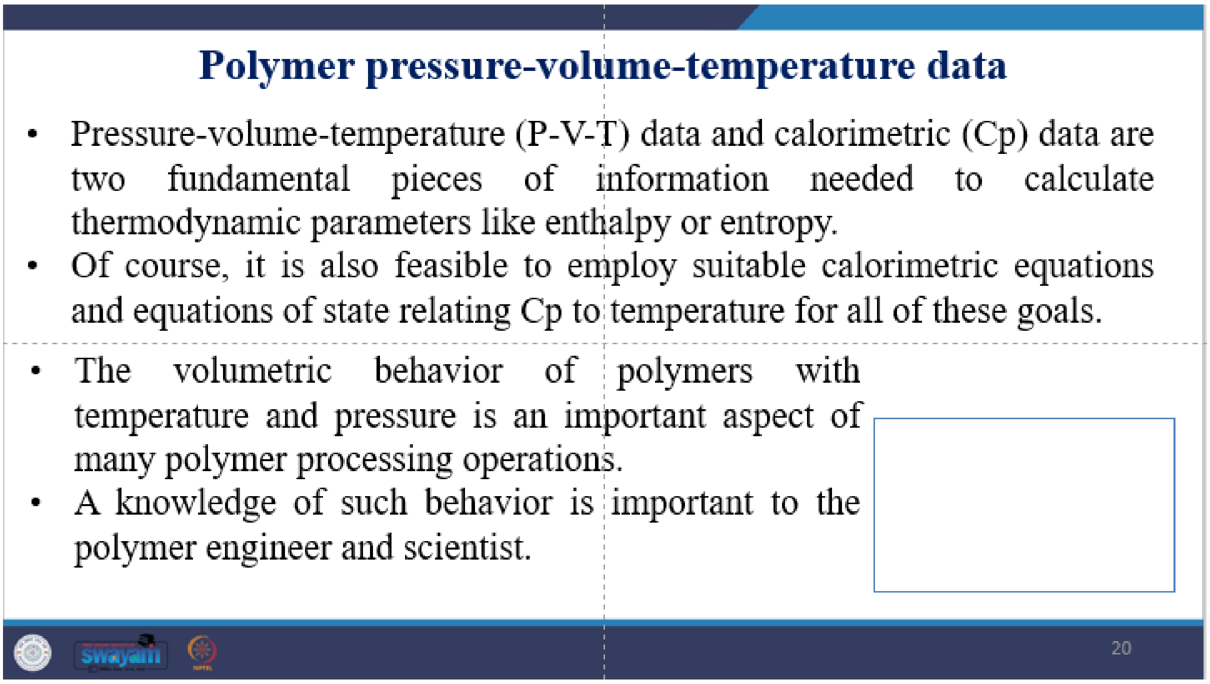
$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dS = \frac{C_P}{T} dT$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dS = -\left(\frac{\partial V}{\partial T}\right)_P dP$$

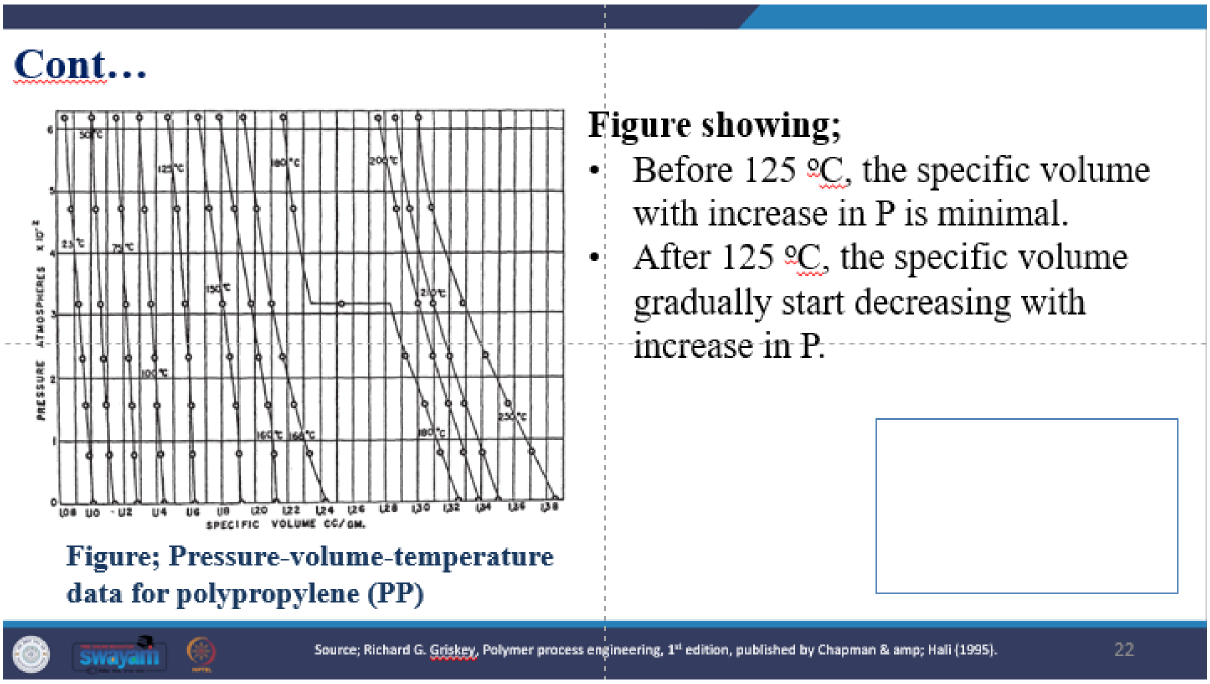
So, therefore, the pressure volume temperature these data are quite important and these data are quite important to measure because for the rest of the data like enthalpy, entropy other things you need to have a correlation which can be developed through the special volume and temperature data. Now this calorimetric data again the Cp data or Cv data these are again very important and these two PVT data and the calorimetric data are the two fundamental pieces of information which need to calculate the thermodynamic parameters like enthalpy, entropy all those things. Now it is also feasible to employ the suitable calorimetric equations and equation of state this is relating to Cp or temperature for all these goals. Now the volumetric behaviour of polymers now sometimes the temperature and pressure is an important aspect of many polymer processing equations. So, therefore, such behaviour is important for any kind of a polymer engineer or scientist.



Polymer pressure-volume-temperature data

- Pressure-volume-temperature (P-V-T) data and calorimetric (Cp) data are two fundamental pieces of information needed to calculate thermodynamic parameters like enthalpy or entropy.
- Of course, it is also feasible to employ suitable calorimetric equations and equations of state relating Cp to temperature for all of these goals.
- The volumetric behavior of polymers with temperature and pressure is an important aspect of many polymer processing operations.
- A knowledge of such behavior is important to the polymer engineer and scientist.

Now here we have depicted some plots for actual PVT data of various polymeric systems. Now depending upon the values of temperature and pressure we can calculate the specific volume of the material. This particular figure is showing the increase in the temperature the specific volume of a polyethylene marginally this changes with increase in pressure and the usefulness of this particular data is that beforehand if you go for any kind of a polymeric process or you are going for like extrusion or if you are going for any kind of a moulding all these things this kind of a behaviour because there will be a continuous rise in the temperature. So, this particular behaviour how much volume change and how much because of the volume change some sort of the pressure change may occur. So, all these kinds of information is extremely important in these aspects.



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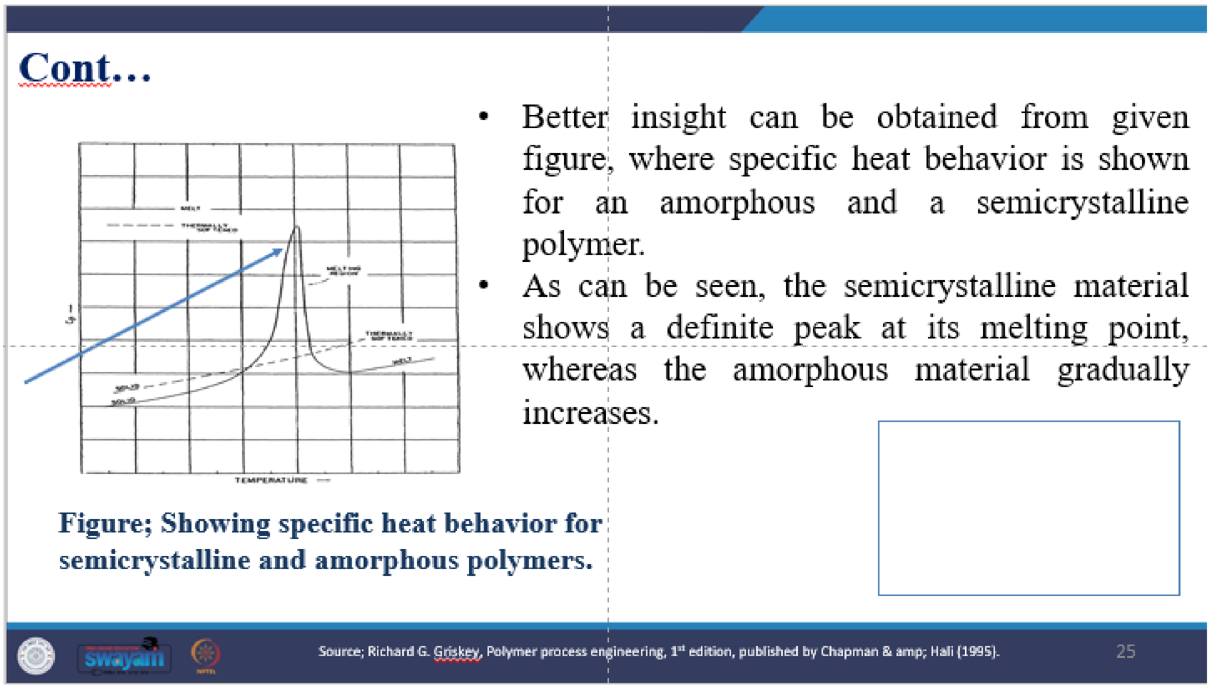
Figure; Pressure-volume-temperature data for polypropylene (PP)

Figure showing;

- Before 125 ºC, the specific volume with increase in P is minimal.
- After 125 ºC, the specific volume gradually start decreasing with increase in P.

Source; Richard G. Griskey, Polymer process engineering, 1st edition, published by Chapman & amp; Hall (1995).

Now if we see that before 125 degree Celsius that is a limiting temperature a specific volume with increase is in pressure is minimum after say 125 degree Celsius the specific volume gradually starts decreasing with increase in pressure. So, at constant pressure the specific volume is directly proportional to the melt temperature and this is why that is why the determining how effectively control of injection speed in the injection moulding machine and the switch over position in order to stabilize the pressure curve is very important and the knowledge about all these curves beforehand is extremely crucial and useful. The solid polymers these can be broadly classified in two general areas which discussed in the some of the lecture like amorphous and a semi crystalline. The semi crystalline polymers they exhibit a melting point and form melts. The amorphous polymer does not melt but only thermally soften.



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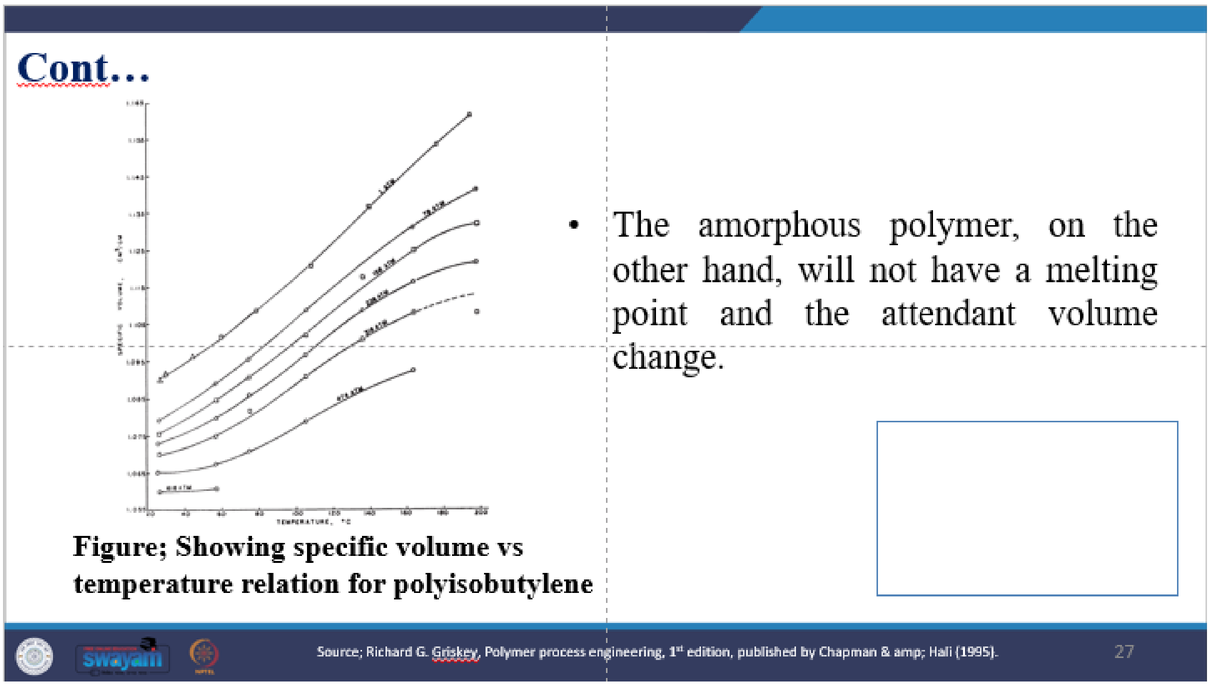
- Better insight can be obtained from given figure, where specific heat behavior is shown for an amorphous and a semicrystalline polymer.
- As can be seen, the semicrystalline material shows a definite peak at its melting point, whereas the amorphous material gradually increases.

Figure; Showing specific heat behavior for semicrystalline and amorphous polymers.

Source; Richard G. Griskey, Polymer process engineering, 1st edition, published by Chapman & amp; Hall (1995).

So, the better inside see again we are going to discuss the temperature behaviour of these polymers semi crystalline and amorphous polymers. So, before better inside this can be obtained and this is given in this particular figure where the specific heat behaviour for any particular polymer for an amorphous or crystalline polymer is given. As you can see here the semi crystalline material shows a defined definite peak at its melting point whereas the amorphous polymer material gradually increases. Now similarly the semi crystalline material this will undergo a significant volume change at constant temperature for a given pressure. So, such an occurrence is the first order transition point.

Now this particular figure refers the volume change at constant temperature for nylon. Another if you take the polyisobutylene this is the effect of specific volume versus temperature. So, the amorphous polymer on the other hand will not have the melting point and attendant volume change. So, you can see the behaviour of these curves. So, all polymers they do undergo second order transition which occurs when the volume temperature curve at a given pressure undergoes a discontinuity but not a volume change at constant temperature.



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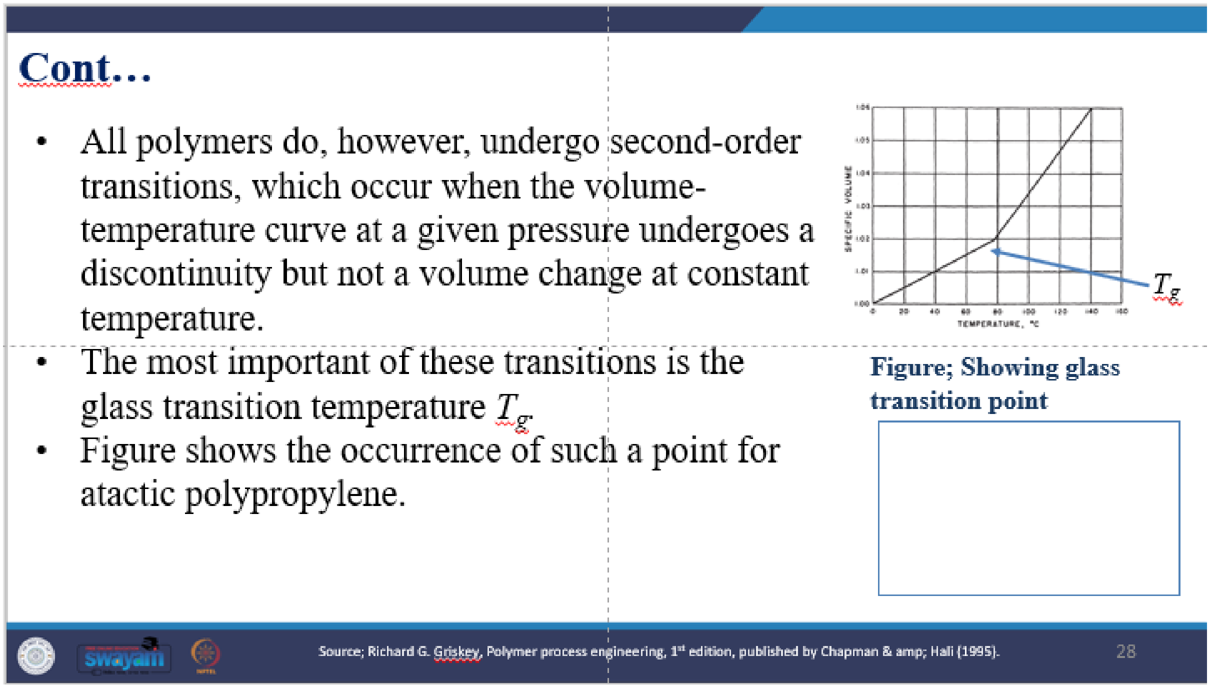
- The amorphous polymer, on the other hand, will not have a melting point and the attendant volume change.

Figure; Showing specific volume vs temperature relation for polyisobutylene

Source; Richard G. Griskey, Polymer process engineering, 1st edition, published by Chapman & amp; Hall (1995).

So, the most important of these transitions in the glass transition temperature because ultimately it reflects the molecular weight distribution and several properties are attributed to this glass transition temperature. Now this particular figure shows the occurrence of such point of atactic polypropylene. Now here you see this is the glass transition temperature. So, the glass transition temperature again in a modified form that represent the point at which polymer segments here this go only the vibrational motion that is the frozen in the glassy state to at a first short range and related long-range diffusional motion. This change is usually marked by significant reduction in the modulus of elasticity of the polymer.



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- All polymers do, however, undergo second-order transitions, which occur when the volume-temperature curve at a given pressure undergoes a discontinuity but not a volume change at constant temperature.
- The most important of these transitions is the glass transition temperature T_g
- Figure shows the occurrence of such a point for atactic polypropylene.

Figure; Showing glass transition point

Source; Richard G. Griskey, Polymer process engineering, 1st edition, published by Chapman & amp; Hall (1995).

Now here you see that the second order transition this can and do occur in polymers which is represented in this particular figure. Here the pressure volume temperature data this shows the discontinuities for the solid polymer and that cannot be attributed to the glass transition temperature. So, the behavior represents the unknown second order transition. Now incidentally the shift of this discontinuity with pressure is about say 0.016 degree Celsius per atom here you see which is compared to a general range of such shift say 0.

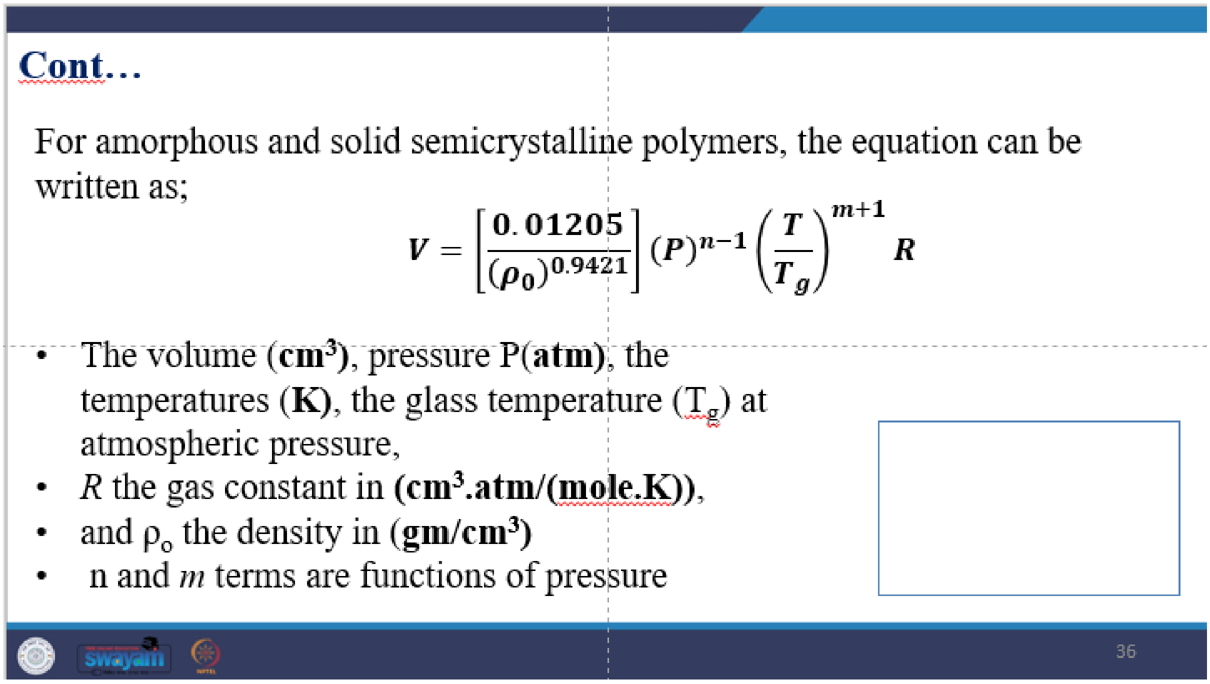
013 to 0.018 degree Celsius. Now let us talk about the equation of state. Now equation of state they play a very vital role and all of us are aware about the equation of state pertaining to the gaseous systems like PV is equal to nRT this PV is equal to nRT is again the equation of state. So, once you have a pressure volume data pressure volume temperature data this is the equation of state can be generated and it gives the perfect you can say the knowledge about the particular state in the polymer possesses. So, the real experimental pressure volume data they are the most effective way to provide this particular information. Sometimes you need to refer the suppose a particular system moves from this state to this state in that case you need to have a equation that reflects that how gradually the system changes and for this particular purpose the pressure volume temperature data sometimes empirical data and sometimes experimental data.

So, if you have some real experimental data they are very useful to predict the state of that particular polymer mass at appropriate time and temperature and pressure. So, this information is sometimes is not accessible and also difficult to ascertain. Now as a result the necessary equation of a state must be created because every time you must you may not have a readymade equation. So, therefore, the sum of the equation must be created. Now these equations enable accurate interpolation of already present data.

Now the equation of a state should meet certain criteria in case of polymer. Now these criteria include the equation must be applicable over wide range of temperature and pressure. If possible, the equation should be generalized. The equation should apply to a large number of different polymers rather than one particular polymer. Now the equation should be such that it can be used to predict the behavior of polymers for which no pressure volume temperature data available.

Ideally, we should be able to calculate pressure volume temperature data for a polymer where only easily measured physical properties are known like glass transition temperature or glass temperature at atmospheric pressure, melting temperature at atmospheric pressure, density at room temperature and atmospheric pressure. So, all equation of a state has their merits. It is recommended that the two-equation based on corresponding state theory be used. The reason is that these represent the generalized equation that depend only on a set of common parameters and on easily accessible data like polymer density at room temperature and atmospheric pressure, glass transition temperature at atmospheric pressure. Now there are because we are discussing two classes of polymer like amorphous polymer and solid semi crystalline polymer.

So, sometimes some of equation may be very useful for predicting these data. So, for amorphous and semi-crystalline polymers, this equation can be represented as V is equal to 0.01205 rho naught to the power 0.9421. So, this is the equation that we are going to get and P to the power n minus 1 T over Tg m plus 1 R.



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For amorphous and solid semicrystalline polymers, the equation can be written as;

$$\boldsymbol{V = \left[\frac{0.01205}{(\rho_0)^{0.9421}}\right](P)^{n-1}\left(\frac{T}{T_g}\right)^{m+1} R}$$

- The volume (**cm^3**), pressure P(**atm**), the temperatures (**K**), the glass temperature (T_g) at atmospheric pressure,
- *R* the gas constant in **(cm^3.atm/(mole.K))**,
- and ρ_o the density in **(gm/cm^3)**
- n and *m* terms are functions of pressure

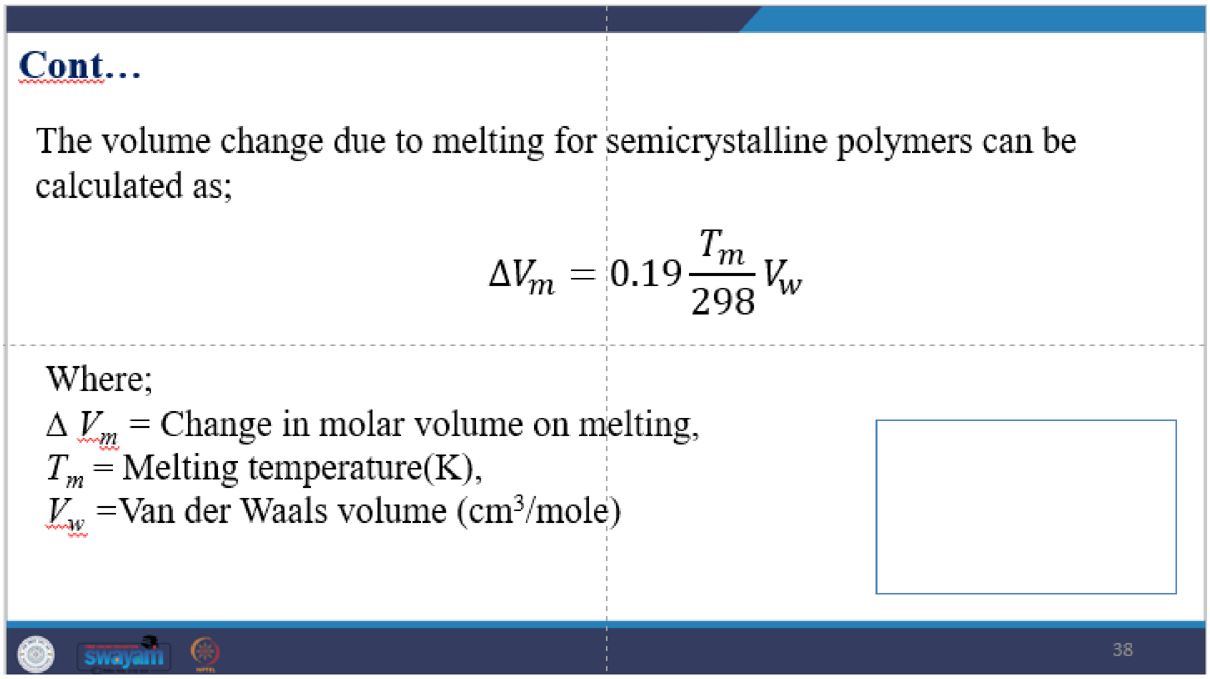
$$\boldsymbol{V = \left[\frac{0.01205}{(\rho_0)^{0.9421}}\right](P)^{n-1}\left(\frac{T}{T_g}\right)^{m+1}}$$

Now the volume this is represented in a centimeter cube, and pressure is represented in the atmosphere. The temperature is represented in Kelvin and the glass transition temperature at atmospheric pressure. R is usually at atmospheric our gas constant and which is having the units of cubic centimeter atmosphere over mole per Kelvin and rho naught is the density which is represented in gram per centimeter cube, and n and m are the terms they are the functions of pressure. Now, similarly for molten semi-crystalline polymers, the relation can be represented as V is equal to k Tover Tg to the power x P to the power y. Here x and y they are the function of pressure while k is the function of rho naught with units of centimeters per over gram per atom.

$$V = K\left(\frac{T}{T_g}\right)^{x} P^{y}$$

Now the volume change due to the melting of semi crystalline polymers semi crystalline polymers can be calculated as delta v m because the volume change whenever you heat the segment then obviously there may be a change in the volume or if you cool down the polymeric mass then there may be certain contraction. So, it is quite evident that you need to calculate the volume change. So, delta Vm is equal to 0.19 t m over 298 Vw where delta Vm is equal to the change in molar volume on melting Tm is the melting temperature which is represented as Kelvin and Vw is equal to 0.19 molar volume on melting v wander was volume centimeter cube per mole.

$$\Delta V_m = 0.19 \frac{T_m}{298} V_w$$



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The volume change due to melting for semicrystalline polymers can be calculated as;

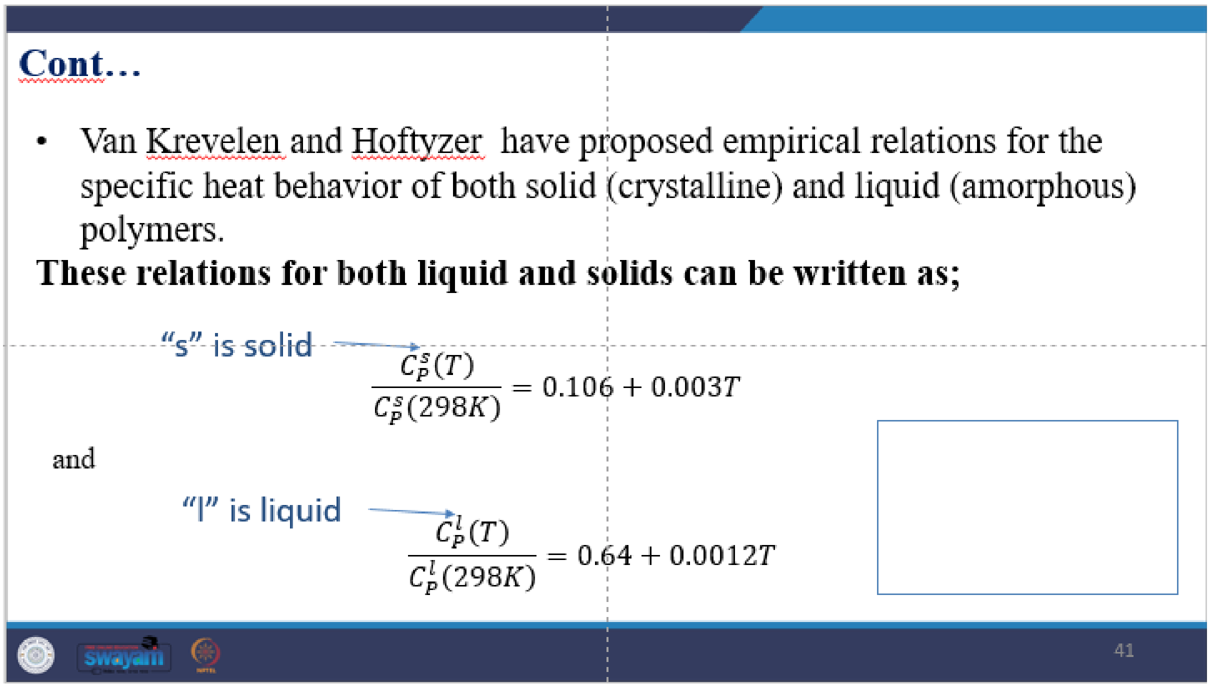
$$\Delta V_m = 0.19 \frac{T_m}{298} V_w$$

Where;
ΔV_m = Change in molar volume on melting,
T_m = Melting temperature(K),
V_w =Van der Waals volume (cm^3/mole)

Now data from the polymer calorimetry they are crucial for determining the thermodynamic properties as well as eventually for the design objectives. So, once you design any kind of a polymeric system then it is quite essential to have this kind of a data. Now it is equally critical to offer suitable correlations when the experimental points they scare and non-existent in order to estimate such data. Now let us talk about the correlation for polymer calorimetry and latent heat data. Whenever possible actual experimental calorimetry data should be used frequently however this cannot be done every time we cannot go for this kind of a calorimetry data.

In such situation it become necessary to estimate the polymeric data with the help of some appropriate correlation. So, the generation of these correlation is extremely important. So, some of the scientists they have proposed the empirical relation for the specific heat behaviour for both crystalline and amorphous polymer. So, these relations for both liquid and solid this can be written as CP S (T) over 298 kelvins, this is the standard notation: 0.

106 plus 0.003T. Here, 'S' is for solid, 'S' is solid. Now if we take the liquid segment into the consideration then Cp l T over Cp l 298 which is 0.64 plus 0.0012 T this is for the liquid. Now here the Cp for solid 298 kelvin and Cp for liquid they are the Cp values which is calculated at 298 kelvin and the calculated from the group contribution of the various organic group of the polymer, and T is obviously in kelvin. So, the specific heat values of amorphous polymer is given as Cp crystalline is equal to Cp for solid plus Cp for liquid 1 minus x, where 'x' is the degree of crystallinity.



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- Van Krevelen and Hoftyzer have proposed empirical relations for the specific heat behavior of both solid (crystalline) and liquid (amorphous) polymers.

These relations for both liquid and solids can be written as;

“s” is solid

$$\frac{C_P^s(T)}{C_P^s(298K)} = 0.106 + 0.003T$$

and

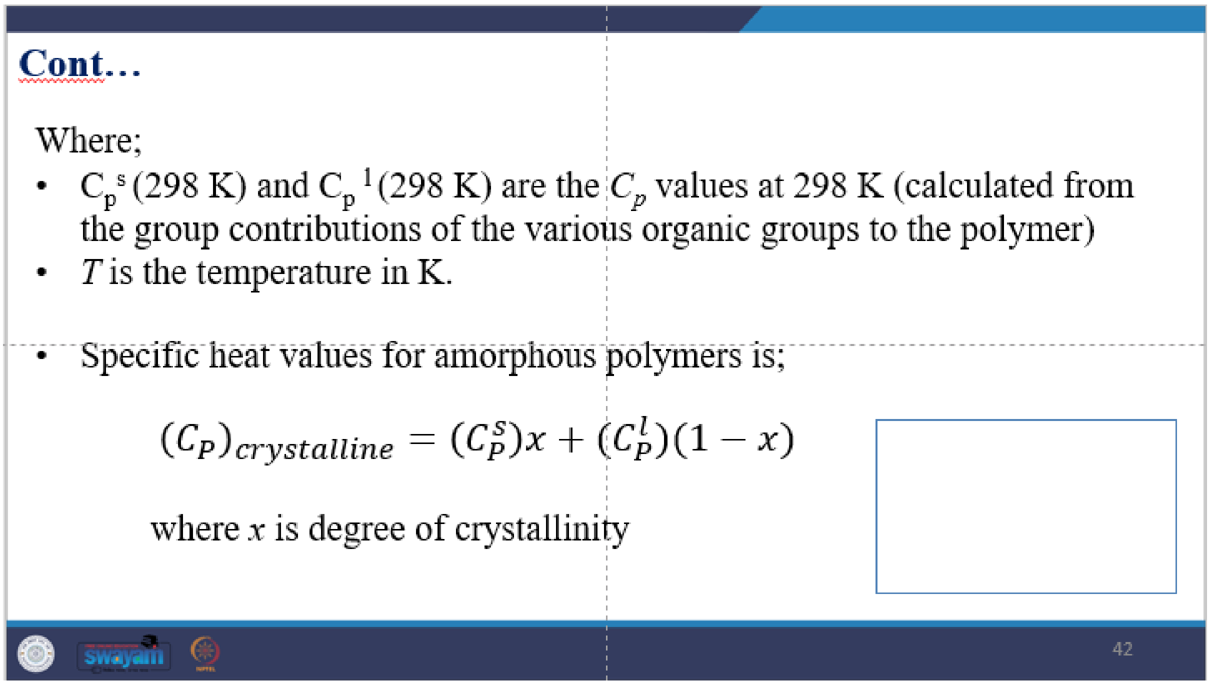
“l” is liquid

$$\frac{C_P^l(T)}{C_P^l(298K)} = 0.64 + 0.0012T$$

$$\frac{C_P^s(T)}{C_P^s(298K)} = 0.106 + 0.003T$$

$$\frac{C_P^l(T)}{C_P^l(298K)} = 0.64 + 0.0012T$$

Now additional correlations they have been developed over the period of time for amorphous and molten polymers and other scientists they show that the Cp data for methacrylate polymers could be correlated using the form of Coates equation originally developed for the organic liquid. Now the similar scientist they gave a rough approximation of a latent heat of a fusion. Now here, this can be represented as delta Hm over Cp for liquid 298 kelvin is equal to 0.55 Tm minus Tg where delta Hm is the latent heat of fusion joule per kilogram Cp for liquid at 298 kelvin, then T joule per kilogram kelvin Tm is equal to melting temperature which is represented in kelvin and Tg is the glass transition temperature in kelvin. So, dear friends in this particular segment we started the thermodynamic behavioral study of polymeric system and in this particular aspect we discussed the PVT behavior, we discussed couple of thermodynamic law and how these laws are applicable.



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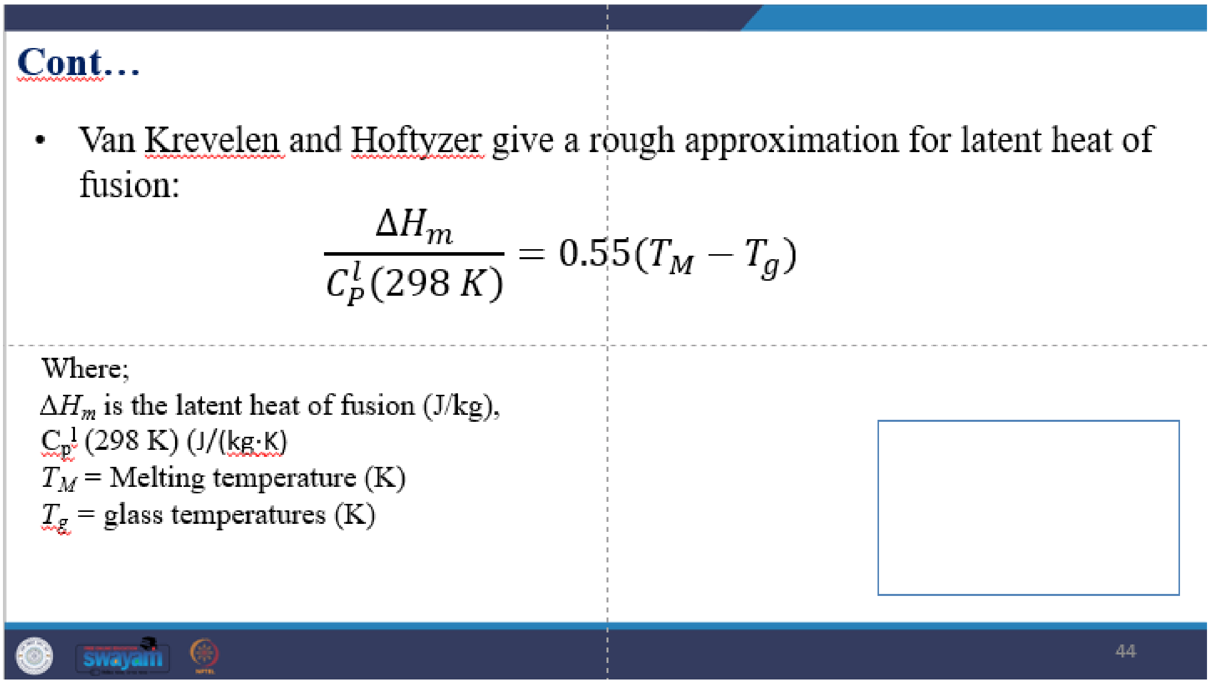
Where;

- $C_p^{\,s}$(298 K) and $C_p^{\,1}$(298 K) are the C_p values at 298 K (calculated from the group contributions of the various organic groups to the polymer)
- T is the temperature in K.
- Specific heat values for amorphous polymers is;

$$(C_P)_{crystalline} = (C_P^s)x + (C_P^l)(1-x)$$

where x is degree of crystallinity

$$(C_P)_{crystalline} = (C_P^s)x + (C_P^l)(1-x)$$



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- Van Krevelen and Hoftyzer give a rough approximation for latent heat of fusion:

$$\frac{\Delta H_m}{C_P^l(298\ K)} = 0.55(T_M - T_g)$$

Where;

ΔH_m is the latent heat of fusion (J/kg),

$C_p^{\,l}$ (298 K) (J/(kg·K)

T_M = Melting temperature (K)

T_g = glass temperatures (K)

$$\frac{\Delta H_m}{C_P^l(298\ K)} = 0.55(T_M - T_g)$$

Apart from this we discussed about the some of the more thermodynamic character with the different graphs that how these thermodynamic properties play a vital role in deciding the various properties of the polymer especially for the end properties and how important these thermodynamic properties for determination of end properties and the life cycle assessment of all these polymers. For your convenience we have enlisted different reference which you can use if you need. Thank you very much.