Introduction to Aerospace Propulsion

Prof. Bhaskar Roy
Prof. A. M. Pradeep
Department of Aerospace Engineering

Indian Institute of Technology, Bombay
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Thermodynamic property relations, Jacobean & Legendre transformations, Maxwells' equations

Hello and welcome to lecture 19 of this lecture series on introduction to aerospace propulsion. So, over the last several lectures we have had some discussions on fundamental aspects of thermodynamics like the laws of thermodynamics and properties and so on. Also, application of thermodynamic principles to actual applications like in cycle analysis and so on. For last 2, 3 lectures, we were discussing about the various power cycles which are used commonly; used in day-to-day applications. We had looked at the basic thermodynamic principles behind these cycles and also what are the small modifications that can be made which can lead to improvement in the efficiency of these cycles. So, these were some of the aspects that were discussed in the last few lectures.

In today's lecture what we are going to take up is a very different topic called… together it is not to do with thermodynamic cycle analysis and so on but, what we shall be discussing today are some very basic thermodynamic relations which are commonly used in analysis of engineering systems. And, some of these topics are very important in analysis of complex thermodynamic systems. So, let us take a look at what we shall be discussing in today's lecture.

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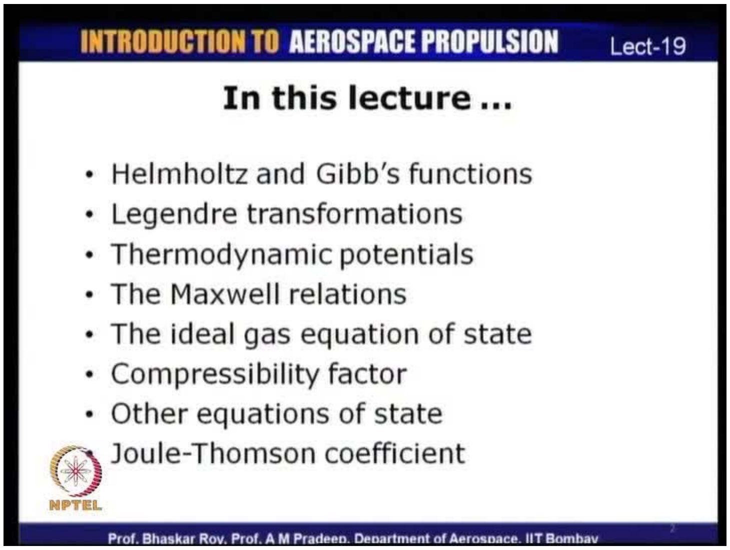

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

In this lecture ...

- Helmholtz and Gibb's functions
- Legendre transformations
- Thermodynamic potentials
- The Maxwell relations
- The ideal gas equation of state
- Compressibility factor
- Other equations of state
- Joule-Thomson coefficient

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We shall be talking about what are known as the Helmholtz and the Gibbs functions and then, we shall be discussing about what are meant by Legendre transformations and as you apply Legendre transformation to certain equations we get what are known as the thermodynamic potentials. Then we will take up a very important set of relations known as the Maxwell relations who play a very significant in thermodynamic cycle analysis and otherwise, we will spend some time on discussing about the ideal gas equation of state and also subsequently, what is meant by the compressibility factor.

We will then take up the other equations of state which are basically modifications of the ideal gas equation states to make it more realistic and towards the end of the lecture, we will be discussing about the Joule Thomson coefficient or the Joule Thomson effect which is basically applied for fluid flows through a throttling device or a throttling process. Now, if you recall several lectures earlier we had discussed about what are known as combination properties. Combination properties are those which are basically a set of different properties which put together have certain thermodynamic significance. One such property which we had discussed was known as the enthalpy.

Enthalpy was defined as the sum of the internal energy plus the product of pressure and specific volume. So, specific internal energy u plus p v is equal to the specific enthalpy; so this was the basic definition of enthalpy which is basically a combination property.

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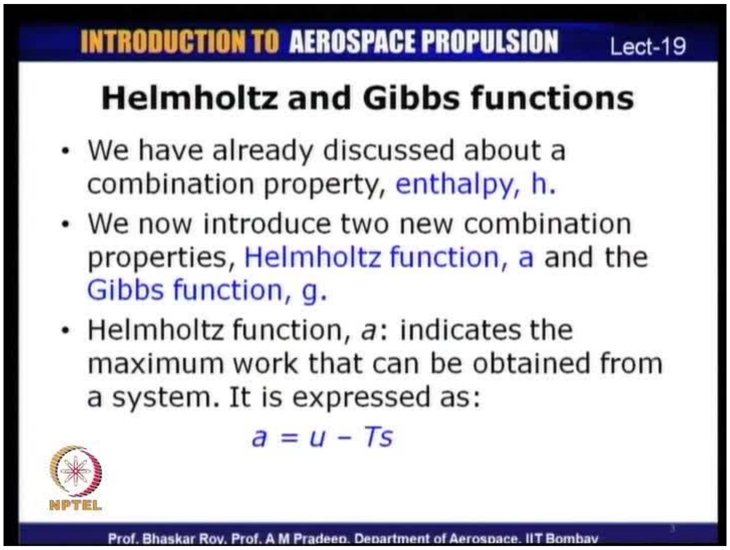

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Helmholtz and Gibbs functions

- We have already discussed about a combination property, enthalpy, h.
- We now introduce two new combination properties, Helmholtz function, a and the Gibbs function, g.
- Helmholtz function, *a*: indicates the maximum work that can be obtained from a system. It is expressed as:

$$a = u - Ts$$

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Today, we will discuss about 2 more combination properties which are known as the Helmholtz function and the Gibbs function. So, let us take a look what these functions are and what their significance are.

So we went to introduce 2 combination properties. First one is known as the Helmholtz function which we will define or denote by a letter a. Helmholtz function is basically an indication of the maximum work that can be extracted from a particular system. We have already discussed about what is the maximum work; what do you mean by useful work? what is known as irreversibility, etcetera and so, based on those definitions or concepts what we shall define today is what is known as the Helmholtz function.

So Helmholtz function by definition is, it basically indicates the maximum work that can be obtained from a system. So, enthalpy is something which we have already discussed; it is a combination property; again, it indicates the work content or energy content of a system.

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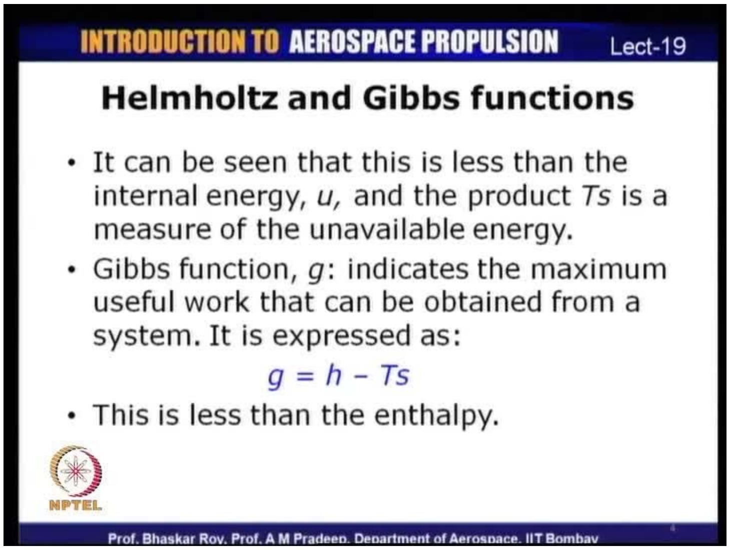

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Helmholtz and Gibbs functions

- It can be seen that this is less than the internal energy, *u*, and the product *Ts* is a measure of the unavailable energy.
- Gibbs function, *g*: indicates the maximum useful work that can be obtained from a system. It is expressed as:

$$g = h - Ts$$

- This is less than the enthalpy.

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So, Helmholtz function by definition is u minus Ts where u is the internal energy and Ts is product of temperature - the absolute temperature and the entropy so this is by definition known as the Helmholtz function.

So, what we can immediately see is that Helmholtz function basically gives us an idea of how much is the internal energy; what is the amount of maximum energy that you can get after you deduct the unavailable energy because, the product Ts is basically the measure of the unavailable energy or the irreversibility which we had defined earlier. So, difference between the internal energy and the unavailable energy is basically the Helmholtz function and so it gives us an idea about the maximum work that can be extracted from a particular system.

The other combination property is known as the Gibbs function. Now, Gibbs function is again very similar to that of Helmholtz function but, it indicates the maximum useful work that can be obtained from a system. Unlike Helmholtz function which was just the indication of the maximum work, Gibbs function gives an idea of maximum useful work that can be extracted from a system. So Gibbs function g - it is denoted by letter g; g is equal to h minus Ts. So, here we are directing the irreversibility or the unavailable energy which is product of T, absolute temperature T and the entropy s from the enthalpy.

So Gibbs function is less than enthalpy;. Helmholtz function is less than the internal energy. So these are 2 functions which we shall be using in today’s discussion. We will also be using, making use of the other equations which were known as the Tds equations we had derived earlier. We will also be using those Tds equations in some of the analysis today and so what we will do in fact, the 2 Tds equations which we had defined earlier and these 2 equations for the Helmholtz function and the Gibbs function all the 4 put together are actually known as the Gibbs equation.

So, the Tds equation and the 2 equations we had defined today for one is for Helmholtz function; the other is for the Gibbs function; all of them put together are classified as the Gibbs equation.

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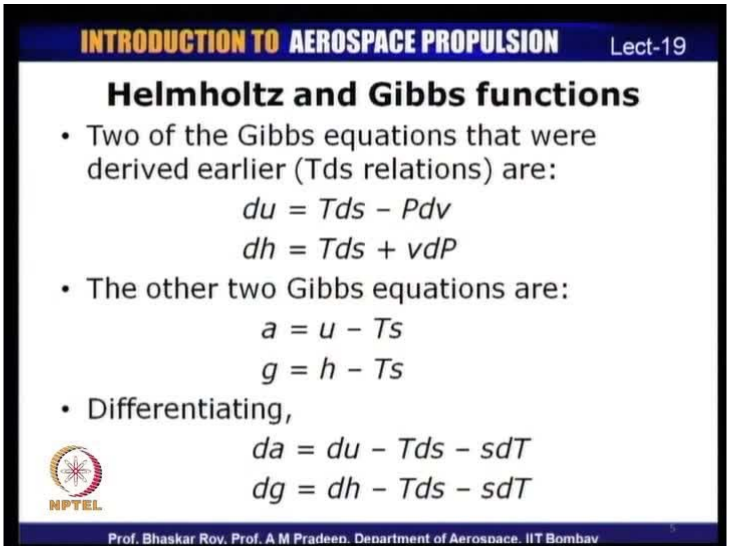

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Helmholtz and Gibbs functions

- Two of the Gibbs equations that were derived earlier (Tds relations) are:

$$du = Tds - Pdv$$
$$dh = Tds + vdP$$

- The other two Gibbs equations are:

$$a = u - Ts$$
$$g = h - Ts$$

- Differentiating,

$$da = du - Tds - sdT$$
$$dg = dh - Tds - sdT$$

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So, two of the equations which we had derived earlier, one is du is equal to Tds minus Pdv and dh is equal to Tds plus vdP. So, these are 2 equations which we had at that time defined as the Tds relation. The two other Gibbs equations are a is equal to u minus Ts and g is equal to h minus Ts which is what we had defined today.

Let us differentiate these 2 Gibbs equations. If you differentiate we get da is equal to du minus Tds minus sdT; similarly, dg is equal to dh minus Tds minus sdT. So these are now 4 differential equations one is in terms of the internal energy; one is in terms of the enthalpy and one is in terms of the Helmholtz function and the last one is in terms the Gibbs function. So these are the 4 different differential equations which we have which relates a set of properties of a system; set of important properties of a system like the temperature the pressure the entropy and volume and so on. So, these properties are related in terms of certain combination properties like enthalpy Helmholtz function and the Gibbs function.

So what we will discuss next is that it is possible for us to express some of these functions or some of these terms in a, in the form of another set of terms by what are known as Legendre transformations. That is, you can make certain you can map or transform a function which is or a property which is a function of a set of properties to another set of properties by using what are known as the Legendre transformations. So, we will use Legendre transforms to basically transform or map a set of parameters or properties from one set to another which basically helps us in certain analysis which we shall be discussing why we are doing this transformation in detail little later on.

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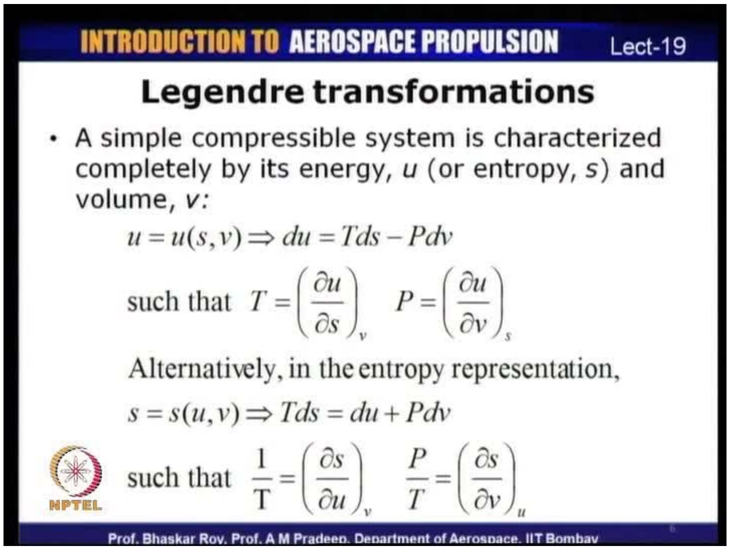

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Legendre transformations

- A simple compressible system is characterized completely by its energy, *u* (or entropy, *s*) and volume, *v*:

$$u = u(s,v) \Rightarrow du = Tds - Pdv$$

such that $T = \left(\frac{\partial u}{\partial s}\right)_v \quad P = \left(\frac{\partial u}{\partial v}\right)_s$

Alternatively, in the entropy representation,

$$s = s(u,v) \Rightarrow Tds = du + Pdv$$

such that $\frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_v \quad \frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_u$

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That once we do this transformation it makes the analysis of thermodynamic systems quite easy; so let us understand what are known as the Legendre transformations. We know that a simple compressible system which is basically a system which is completely defined from the state postulate which says that a simple compressible system can be completely defined or characterized by 2 independent and intensive properties.

And so and… This is the state postulate and a simple compressible system is one which is divoid of any effects of magnetic effects or gravity and so on and so what we have said is that we can actually characterize a simple compressible system completely by using either energy which is internal energy u or entropy s and its volume. So, this is an example; of course, you can also characterize a simple compressible system by another set of properties. Just for an example we are going to take up a compressible system - simple compressible system which we shall characterize by its energy or entropy and the volume which means that u is a function of entropy s and specific volume v which means we have already seen the Tds equation du which basically relates the internal energy entropy and the volume. So, du is equal to Tds minus Pdv; so this is the Tds equation which we had defined such that for constant volume we get T is equal to du by or del u by del s for constant volume. That is if you look at the first Tds equation which is du is equal to Tds minus Pdv, this equation can also be rewritten for constant volume specific volume as T is equal to del u by del s where v is for constant v. Similarly, for constant s we get pressure P is equal to del u by del v at constant s.

So, what it means is that if you take up, if you look at as basic Gibbs equation, one of the Gibbs equations and apply certain boundary conditions, you can express one of the properties in terms of the other two like temperature here has been expressed in terms of the energy and entropy P is in pressure is expressed in terms of energy and the volume. Similarly, let us look at what happens if you were to map the equation for entropy in the same fashion.

Entropy as s is a function of internal energy and the volume. Let us look at another set of Tds; the same equation Tds equation in terms of entropy. So, Tds is equal to du plus Pdv which again by applying similar boundary conditions we get 1 by T is equal to del s by del u at constant v. That is if v is a constant we get 1 by T as del s divided by del u at constant v and similarly, the ratio pressure by temperature P by T is equal to del s by del v at constant u. That is, energy being constant you can express the properties pressure and temperature in terms of the change in entropy with reference to the specific volume the partial derivative of entropy with reference to the partial derivative of the specific volume keeping the energy internal energy constant.

So, what we have basically done is that we can map certain parameters which could be like in the example we have discussed this parameter, set of parameters where the first example was energy. Energy was expressed or can be expressed in terms of entropy and volume and we can correspondingly map the properties like temperature or a pressure in the form of partial derivatives of some of the other properties like energy del u by t was equal to del u by del s at constant v and so on. So you can actually map certain properties important properties of a system in terms of partial derivatives of another set of properties of the same system. So, a Legendre transformation basically helps us in carrying this kind of transformation which will basically help us in certain analysis.

One example I shall give you is that you are very much interested in determining the change in the entropy of a particular process but as we know entropy is not something which you can very easily measure. Entropy is a parameter which is very difficult to measure directly. There are no devices which can actually measure entropy as such but if you are able to express entropy in terms of parameters which can be easily measured or experimentally like temperature or pressure or volume then, it makes analysis a lot simpler because now you have entropy which has been expressed in terms of a set of another parameters like temperature or pressure and they can be measured quite easily. Whereas, entropy on the other hand is not something which you can measure very easily.

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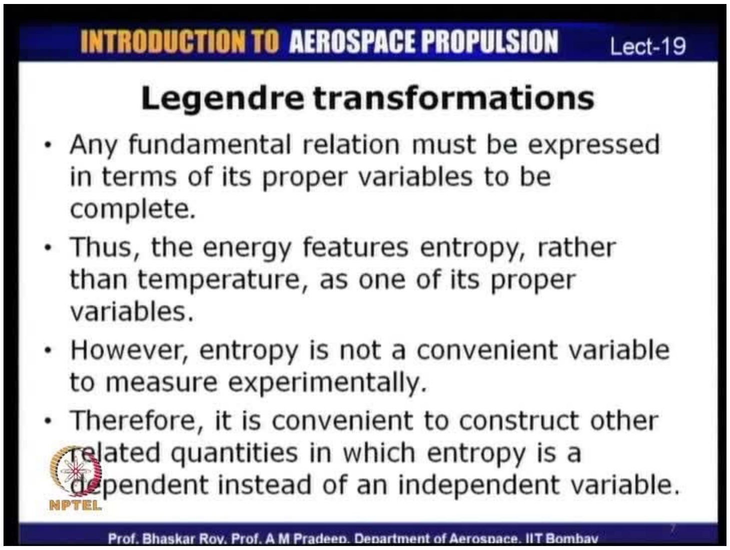

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Legendre transformations

- Any fundamental relation must be expressed in terms of its proper variables to be complete.
- Thus, the energy features entropy, rather than temperature, as one of its proper variables.
- However, entropy is not a convenient variable to measure experimentally.
- Therefore, it is convenient to construct other related quantities in which entropy is a dependent instead of an independent variable.

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And so Legendre transformation helps us in expressing some such parameters in terms of another set of parameters which we can measure easily. So, that is one of the advantages of carrying out this kind of a transformation. If you look at the properties of the, or the advantages of Legendre transformation, Legendre transformation basically we know that any fundamental expression or a relation.

We need to express it in terms of proper variables so the relation is complete which is why energy will always feature entropy. That is, if you are expressing energy internal energy as we did in the example which was expressed in terms of entropy s and volume v but you would rather have temperature as one of the proper variables because basically because entropy is not something that can be easily measured experimentally. Therefore, it is convenient to construct other related quantities in which entropy is a dependent variable instead of an independent variable because, if it is a dependent variable then you can actually express entropy in terms of other parameters which can be measured like temperature and pressure or volume.

Whereas, if it happens to be an independent variable then it means that you will have an expression which relates energy in terms of entropy alone and that is something that you cannot measure easily and that is one of the advantages that you would want to carry out the Legendre transformation. Now, let us also take up an example of let us say the Helmholtz function; we have already had an example for the energy in terms of entropy and volume.

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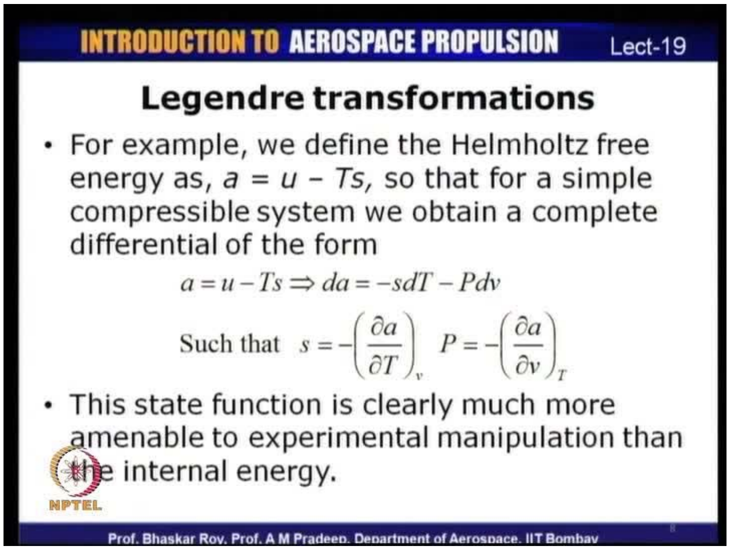

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Legendre transformations

- For example, we define the Helmholtz free energy as, $a = u - Ts$, so that for a simple compressible system we obtain a complete differential of the form

$$a = u - Ts \Rightarrow da = -sdT - Pdv$$

$$\text{Such that} \quad s = -\left(\frac{\partial a}{\partial T}\right)_v \quad P = -\left(\frac{\partial a}{\partial v}\right)_T$$

- This state function is clearly much more amenable to experimental manipulation than the internal energy.

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Let us also look at one example which has Helmholtz function. As the example now we have already defined the Helmholtz function also known as in some books, you will also see Helmholtz function being defined as Helmholtz free energy. So, Helmholtz free energy was defined as a is equal to u minus Ts. Now, if you look at a simple compressible system a is equal to u minus Ts can be written as if you differentiate da is equal to du minus sdT minus Pdv and so on and so, we had already differentiated this a few slides earlier. Now, this can be simplified as da is equal to minus sdT minus Pdv which comes from the Tds equation because da is equal to du minus Tds minus sdT du minus Tds is equal to minus Pdv from the first Tds equation. Therefore, da is equal to minus sdT minus Pdv. Again, if you were to apply the transformation here we get this equation, can be expressed in a different way as entropy s is equal to minus del a by del t at constant v.

Similarly, pressure P is equal to minus del a by del v at constant T. now, what we have here is that entropy; it can actually be expressed as in terms of partial derivatives of the Helmholtz function or the Helmholtz free energy divided by with reference to temperature at constant specific volume. So, here we can, the state function now is much more amenable to express the experimental manipulation than the internal energy because energy or the entropy on the other hand is something that is quite difficult to measure and once you can express the state function in terms of parameters which can be easily measured, that makes thermodynamic analysis a lot simpler because you now have expressed the state variables in terms of parameters which can be easily measured.

So that is why we would like to carry out such transformations for certain parameters which you would like to measure and therefore, you would like to express it in terms of certain functions or parameters which is much more experimentally amenable. So, we will now define what we are going to refer to as the thermodynamic potential so the derivatives that we get from these the transformations are basically referred to as the thermodynamic potential.

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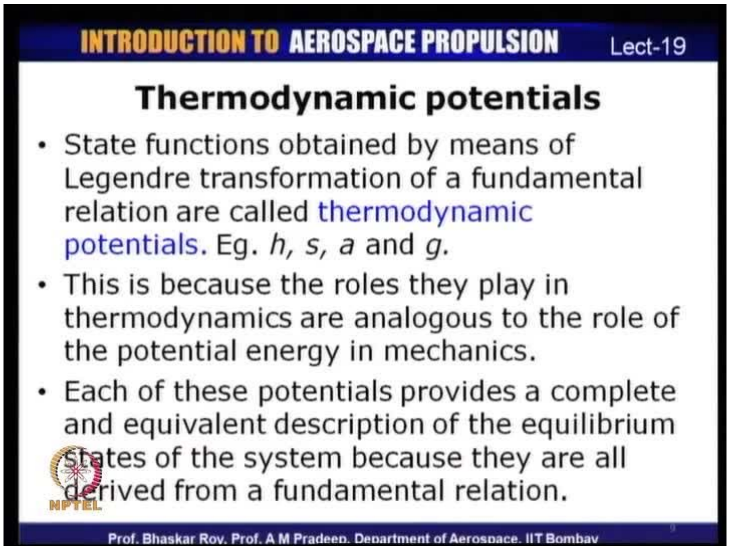

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Thermodynamic potentials

- State functions obtained by means of Legendre transformation of a fundamental relation are called thermodynamic potentials. Eg. *h, s, a* and *g*.
- This is because the roles they play in thermodynamics are analogous to the role of the potential energy in mechanics.
- Each of these potentials provides a complete and equivalent description of the equilibrium states of the system because they are all derived from a fundamental relation.

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State functions which we obtained as a means of or as an outcome of the transformation of the Legendre transformation, are known as the thermodynamic potential. So, thermodynamic potentials examples of thermodynamic potentials are enthalpy; the entropy is also thermodynamic potential the Gibbs function or Gibbs free energy and the Helmholtz function or Helmholtz free energy. So, state functions which we obtain as a consequence of the Legendre transformation, we already seen what is the Legendre transformation which is a set of transformations which we can do to map a set of functions or parameters in terms of other functions or parameters which are much more easier to measure experimentally. So, as you transform or map these parameters from one set of one set to another; we can do that by using the Legendre transformation. So, the state functions or state variables that you get as a consequence of this Legendre transformation are referred to as the thermodynamic potential examples being enthalpy, Gibbs free energy, Helmholtz energy and so on.

Now, why are they thermodynamic potential? Well, they are basically called thermodynamic potential because they look similar to or are analogous to the potential energy which we come across very frequently in mechanics.

So, because of their similarity that is the similarity of these functions, the enthalpy, entropy, free energy and so on, because of their similarity to the potential energy which we come across in mechanics, these are known as the thermodynamic potential because these are potentials which come up in thermodynamic analysis and that is why they are called the thermodynamic potential because of this similarity. The other aspect of the potential is that each of these potentials provide a complete and equivalent description of the equilibrium states of the system; because they are all derived from a fundamental relation we have seen and the enthalpy is derived from a fundamental relation it relates basically the internal energy and product p v which is a very fundamental.

All of these 3 parameters are fundamental parameters and so similarly, the free energy Gibbs free energy or Helmholtz energy they are all derived from certain fundamental relations and so each of these terms will provide a complete description of the equilibrium states of a system, because they all come from a or they are all derived from set of fundamental properties. Now, so we can actually map or carry out the Legendre transformation for different sets of parameters or state variables and derive the corresponding thermodynamic potentials for these kind of, these set of state variables. So, what I will do is I have already explained how to carry out these analyses for some examples like energy or entropy or the Helmholtz free energy. So, with that background you should be able to now calculate or carry out this transformation for other set of parameters or state variables.

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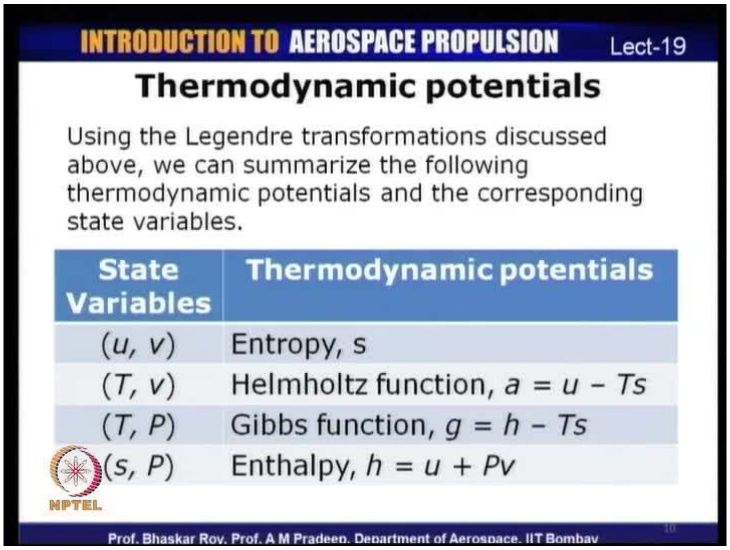

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Thermodynamic potentials

Using the Legendre transformations discussed above, we can summarize the following thermodynamic potentials and the corresponding state variables.

State Variables	Thermodynamic potentials
(u, v)	Entropy, s
(T, v)	Helmholtz function, $a = u - Ts$
(T, P)	Gibbs function, $g = h - Ts$
(s, P)	Enthalpy, $h = u + Pv$

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So let us summarize. I would summarize the use of Legendre transformation for different state variables and the corresponding thermodynamic potentials.

So in the table that is shown here, we have the state variables on the left hand side first column, this is the second column are the thermodynamic potentials. So, we have seen that from the set of state variables u and v that is energy and the specific volume we should be able to derive the thermodynamic potential which is entropy using the Legendre transformation; so this was one example which I had discussed.

The other example I had discussed was the Helmholtz function. That is, you can derive the Helmholtz function which is basically the thermodynamic potential and correspondingly, we can carry out the Legendre transformation from the state variables for temperature absolute temperature T and the specific volume v. So, carrying using these two state variables you can carry out the Legendre transformation for the Helmholtz function. Similarly, we can carry out the transformations for Gibbs function in terms of the state variables temperature T and pressure P for Gibbs function which is g is equal to h minus Ts and for enthalpy, the state variables would be entropy s and the pressure P absolute pressure P where enthalpy is u plus P v.

So, this is just to summarize how you can express different potential thermodynamic potentials as a consequence of using a set of state variables through the Legendre transformation. Thermodynamic potential basically helps us in understanding or equating certain potentials which we also say see in mechanics and so similarly, in thermodynamic analysis we come across certain potentials which are very similar or analogous to the potential energy of mechanics.

Now that we have understood the Legendre transformation and how you can express certain parameters or functions in terms of a set of a different set of parameters which are more amenable to measurements like you can express entropy in terms other set of parameters and so on. So ,we shall now discuss about what are known the Maxwell equations. Maxwell relations or Maxwell equations are basically derived from the Gibbs equations. All the 4 Gibbs equations put together you can carry out the Legendre transformation and derive the Maxwell equation from all these 4 Gibbs equations. So, Maxwell relations basically relates some of the basic properties of a simple compressible system like the pressure, volume, temperature and entropy and we basically get partial derivatives of these properties in terms of the others and this is basically applied for simple compressible systems. But, as we will see little later on that we have we can also derive such equations for non-simple systems which involve electric or magnetic force etcetera and get the corresponding Maxwell's relations for those systems. But, what we will discuss today is only for a simple compressible system that we express these basic properties like temperature, pressure, specific volume, entropy, etcetera in terms of partial derivatives.

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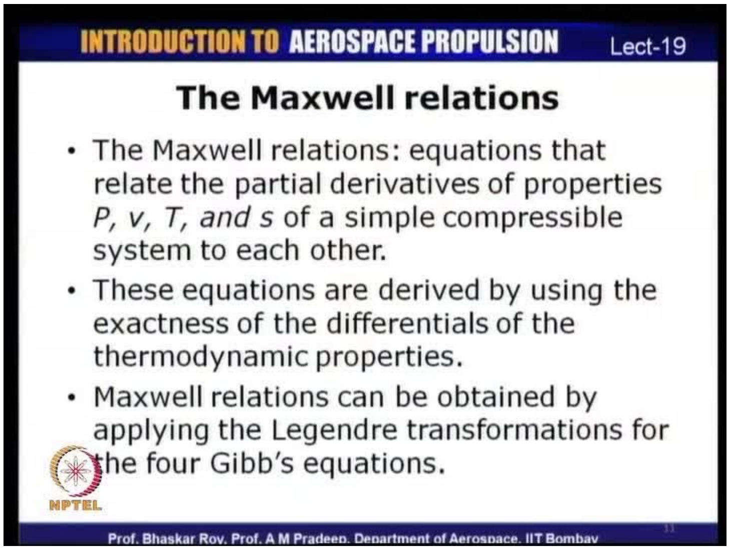

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The Maxwell relations

- The Maxwell relations: equations that relate the partial derivatives of properties *P, v, T, and s* of a simple compressible system to each other.
- These equations are derived by using the exactness of the differentials of the thermodynamic properties.
- Maxwell relations can be obtained by applying the Legendre transformations for the four Gibb's equations.

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So, Maxwell relations are basically equations that relate the partial derivative of properties like pressure, specific volume, temperature and entropy of a simple compressible system to each other that is you would have partial derivatives of pressure in terms of temperature and so on.

Now, we will make use of the fact that all of these properties are basically because they are thermodynamic properties; they are exact differentials. So, these equations will be derived by using exactness of the differentials of these thermodynamic properties.

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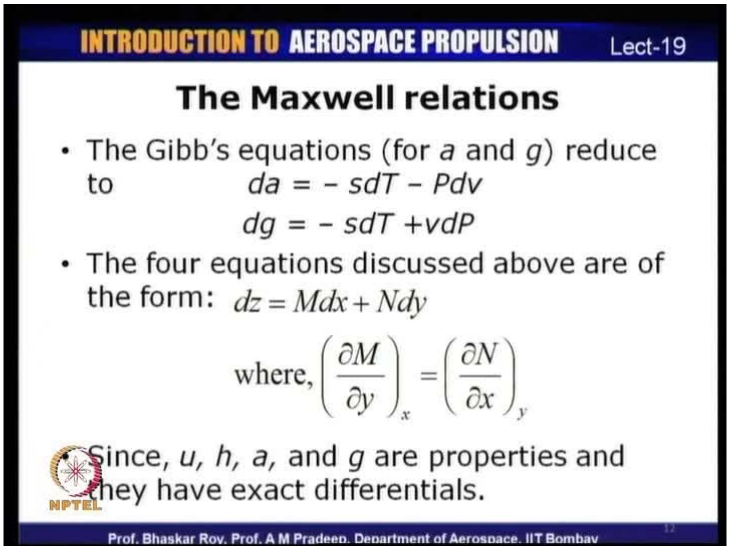

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The Maxwell relations

- The Gibb's equations (for a and g) reduce to $da = -sdT - Pdv$
  $dg = -sdT + vdP$
- The four equations discussed above are of the form: $dz = Mdx + Ndy$

$$\text{where, } \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Since, u, h, a, and g are properties and they have exact differentials.

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So, Maxwell relation basically can be obtained by applying these Legendre transformations to the 4 Gibbs equations and what were those 4 Gibbs equations? We had already discussed about the Tds equations. There are 2 Tds equations: one is in terms of energy u and the other in terms of enthalpy h. In addition to that the other 2 Gibbs equations one is for the Helmholtz function a and the other is for the Gibbs function g.

So, the Gibbs equation can actually be simplified in by using the Tds equations which we get from which we get da is equal to minus sdT minus Pdv; so that is the third Gibbs equation and dg is equal to minus sdT plus Pdv. So, plus dg is equal to minus sdT plus vdP. Now, we have a set of 4 equations all of them put together are known as the Gibbs equations and all these equations if you see carefully they are all of this form which of the general form which is written here as dz is equal to Mdx plus Ndy.

So, this is like a set of exact differentials and if you recall from mathematics which you might have studied earlier on such equations can actually be written in terms of the partial derivatives of these variables here. So, dz is equal to Mdx plus Ndy can be expressed as del M by del y at constant x is equal to del N by del x at y that is these functions that you see here in terms of M and N can be expressed as partial derivatives in this fashion. So, if you have an equation of this form dz is equal to Mdx plus Ndy then it also follows that del M by del y at x is equal to del N by del x at y. now, since all these equations that is the 4 Gibbs equations are in terms of properties of a system like energy enthalpy the Helmholtz function and the Gibbs function which all of which are properties of a system.

They should have exact differentials which means all these 4 equations which we had discussed one is in terms an energy u second is in terms of enthalpy h then the Helmholtz function a and the Gibbs function g all these 4 equations only deal with properties of a system. Therefore, all of these equations should have exact differentials which means all these equations can be expressed in a fashion which was just discussed for a general equation dz is equal to Mdx plus Ndy where M del M by del y at x is equal to del N by del x del N by del y at x.

So, if we were to express all those 4 equations, 4 Gibbs equations and apply the exact differentials for them because all these equations are in terms of properties of a system and if you were to do that then we get a set of four relations which are basically known as the Maxwell equations. So, if we take the equations one by one that is the first Tds equation apply the exact differential property for that second Tds equation and so on; then we get the Maxwell relations which are shown here.

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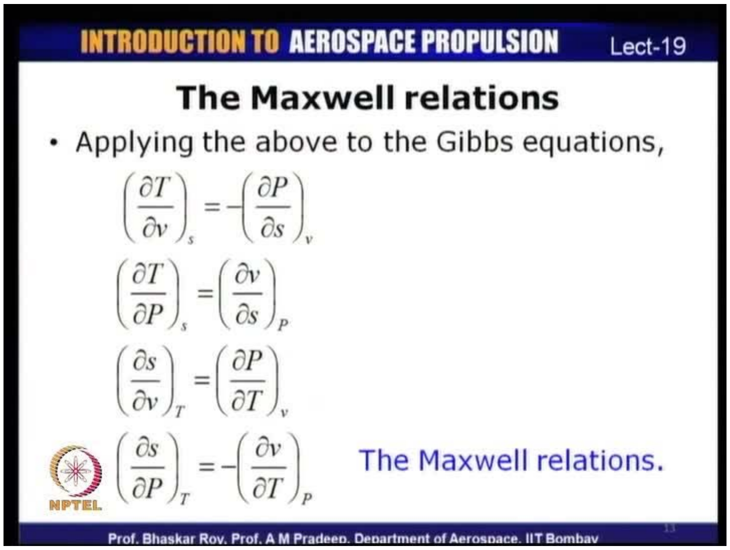

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The Maxwell relations

- Applying the above to the Gibbs equations,

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

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

The Maxwell relations.

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So, applying this property of or identity of exact differentials to the Gibbs equation then we get from the first and from all the 4 Gibbs equations together we get del T by del v at s is equal to minus del P by del s at v. The second Maxwell relation is del T by del P at s is equal to del v by del s at P third Maxwell equation or Maxwell relation is del s by del v at T is equal to del P by del T at v and the last Maxwell relation del s by del P at T is equal to minus del v by del T at P so all these 4 equations are basically known as the Maxwell relations which are basically derived from the Gibbs equations and by applying the exact differentials to all these Gibbs equations.

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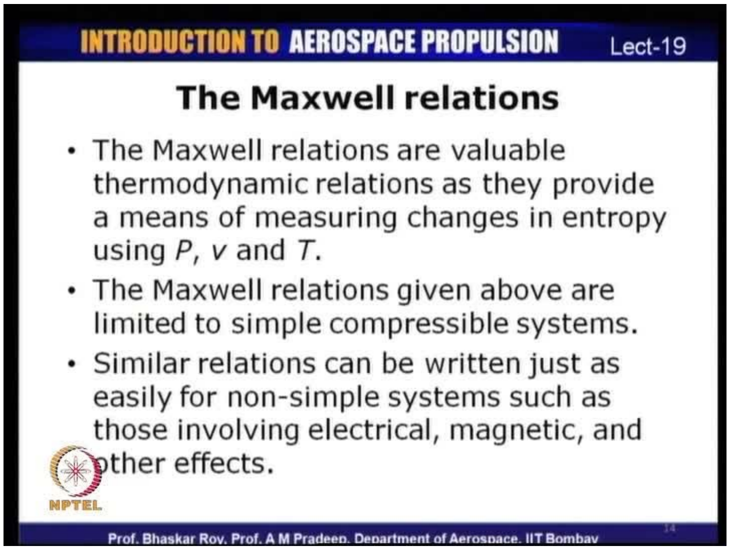

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The Maxwell relations

- The Maxwell relations are valuable thermodynamic relations as they provide a means of measuring changes in entropy using *P*, *v* and *T*.
- The Maxwell relations given above are limited to simple compressible systems.
- Similar relations can be written just as easily for non-simple systems such as those involving electrical, magnetic, and other effects.

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14

Now, what is the significance of Maxwell relation? Now, that we have defined these 4 equations in terms which are basically partial derivatives of the properties expressed in terms of one another.

What is the significance of these Maxwell relations? Basically, Maxwell relations are important thermodynamic relations because they provide a means of measuring changes in entropy using variables which can be easily measured like pressure, volume, temperature, etcetera and the equations that we just discussed or the Maxwell relation which we had discussed is basically limited to simple compressible systems but we should be able to derive similar relations for non-simple systems which involve electric magnetic and other effects and so on. So, Maxwell relations which we discussed though were restricted to simple compressible systems which basically do not have effects of electric magnetic fields and so on. Such equations are also derived for equation or for systems which involve non simple effects like electric magnetic fields.

So what we had discussed were so far were firstly the Gibbs and Helmholtz function then we discussed about the Legendre transformation which helps us in expressing one function in terms of set of another functions which can be easily measured and so on. And, Maxwell relation is basically a consequence of these transformation applied to the Gibbs equations - the 4 Gibbs equations. What we shall discuss next are the equations of states and we will start our discussion with discussing about the ideal gas equation of state and then we will see how you can modify these ideal gas equations of state to include real gas effects.

Now, ideal gas equation of state is something which you are already familiar with and we have used this also in some of the numerical calculations or during our tutorials in some of the earlier lectures where we had assumed that air is an ideal gas for the range of temperatures for which we were carrying out the calculations. So, we had defined ideal gas equation there as Pv is equal to RT. So, that is basic ideal gas equation of state which expresses 2 properties which basically relates 3 properties of the ideal gas pressure, volume and temperature.

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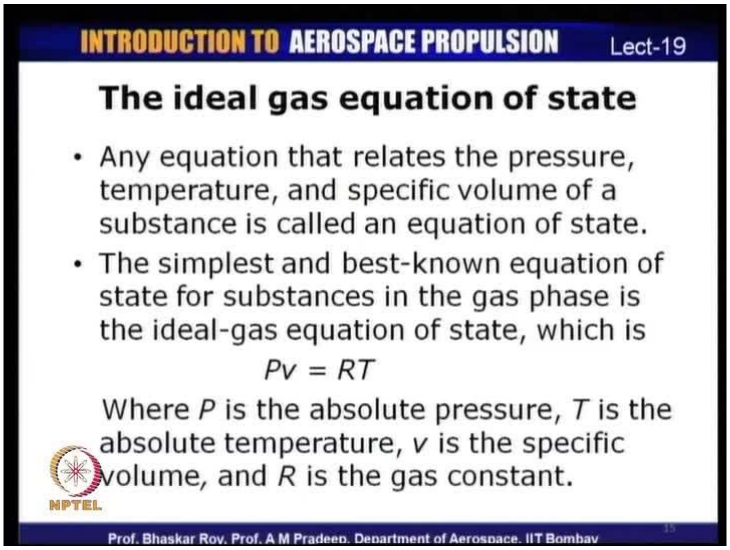

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The ideal gas equation of state

- Any equation that relates the pressure, temperature, and specific volume of a substance is called an equation of state.
- The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state, which is

$$Pv = RT$$

Where P is the absolute pressure, T is the absolute temperature, v is the specific volume, and R is the gas constant.

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Then there is a constant which is known as the gas constant. Now, any equation which basis so, if you look at equation of state you can actually have any equation which relates the pressure, temperature and specific volume of a substance is basically known as an equation of state. Now, the simplest and the best known equation of state which we are aware of so far is the ideal gas equation of state which is Pv is equal to RT.

Now, in this equation the pressure P is the absolute pressure; T is the absolute temperature; v is the specific volume and R is the gas constant for the particular gas we are interested in. For air, we can calculate gas constant by dividing the universal gas constant by the molecular weight of that particular gas. Now, the equation of state we had just discussed is meant for an ideal gas. Now, real gases can deviate substantially from this ideal gas nature depending upon the pressure and temperature that we are dealing with. So, depending upon that, the actual gas behavior can substantially different from that of an ideal gas. So is there a way or is there a method of accounting for this deviation of actual gas from the ideal gas behavior?

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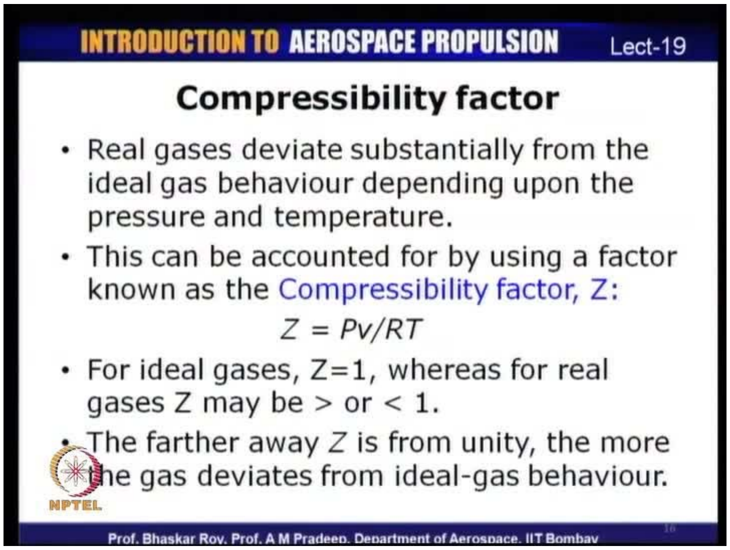

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Compressibility factor

- Real gases deviate substantially from the ideal gas behaviour depending upon the pressure and temperature.
- This can be accounted for by using a factor known as the Compressibility factor, Z:

$$Z = Pv/RT$$

- For ideal gases, Z=1, whereas for real gases Z may be > or < 1.
- The farther away Z is from unity, the more the gas deviates from ideal-gas behaviour.

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16

What we will do now is to define 1 parameter which can partly account for this deviation and this factor we shall define as what is known as the compressibility factor and so compressibility factor is basically defined as the ratio Pv by RT Z is defined as Pv by RT and this is basically known as the compressibility factor. This is primarily meant to account for the deviation of real gas effects from the ideal gas behavior. So, for an ideal gas obviously Z will be equal to 1 and for a real gas Z may be greater than 1 or it may be less than 1 depending on the pressure and temperature at which it is operating.

So the farther away, Z is from unity whether it is less than 1 or greater than 1, the more is the deviation of the gas from the ideal gas behavior. That is, if Z is much less than 1 or Z is greater than 1 it means that, that particular gas is deviating from the ideal gas behavior by that much amount; because for an ideal gas, Z is equal to 1. So, compressibility factor is 1 parameter which can probably account for some of these T l gas effects and this is basically because real gases behave differently at different pressures and temperatures and so which means that, how do you account for this deviation if you have just 1 parameter?

In this case, what we do is that we normalize the pressures and temperatures with reference to the critical pressure and temperature of that particular gas and so, if we let us say normalize pressure with reference to the critical pressure, we get a normalized pressure which we shall now define as what is known as the reduced pressure.

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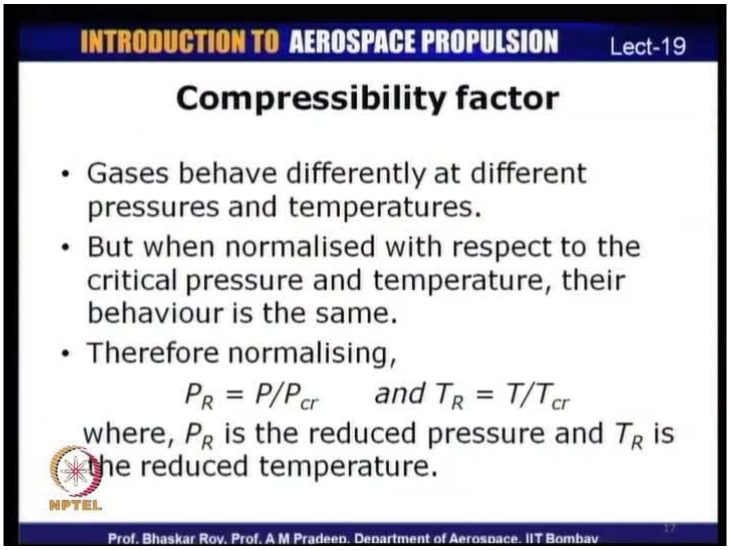
INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Compressibility factor

- Gases behave differently at different pressures and temperatures.
- But when normalised with respect to the critical pressure and temperature, their behaviour is the same.
- Therefore normalising,

$$P_R = P/P_{cr} \quad and \; T_R = T/T_{cr}$$

where, P_R is the reduced pressure and T_R is the reduced temperature.

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Similarly, temperature divided by temperature at the critical state is defined as the reduced temperature. So, when we reduce the temperatures and pressures that is when we normalize pressures and temperature, then the behavior of different gases because now they have already normalized, is basically the same is more or less the same. I will show you one example where we will see that though they are not exactly the same they can, the behavior of different gases can be assumed to be falling the same trend.

So, in order to account for the different behavior of the gases at different pressures and temperatures, we normalize them so the reduced pressure P R is equal to P divided by critical pressure and T R is equal to T divided by the critical temperature.

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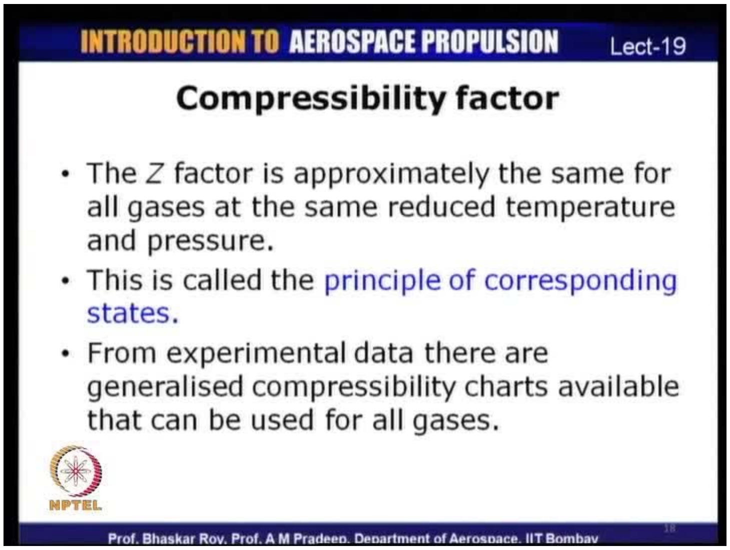

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Compressibility factor

- The Z factor is approximately the same for all gases at the same reduced temperature and pressure.
- This is called the principle of corresponding states.
- From experimental data there are generalised compressibility charts available that can be used for all gases.

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18

Now, if you do that basically what happens is that, the compressibility factor or the Z factor will now be approximately the same for all the gases at the same reduced temperatures and pressures and this is basically known as the principle of corresponding states. That is, once you normalize the pressure and temperature of a particular gas with reference to the critical values, then the compressibility factor for all the gases for the same set of reduced temperatures and pressures will be approximately the same. This is basically the principle of corresponding state.

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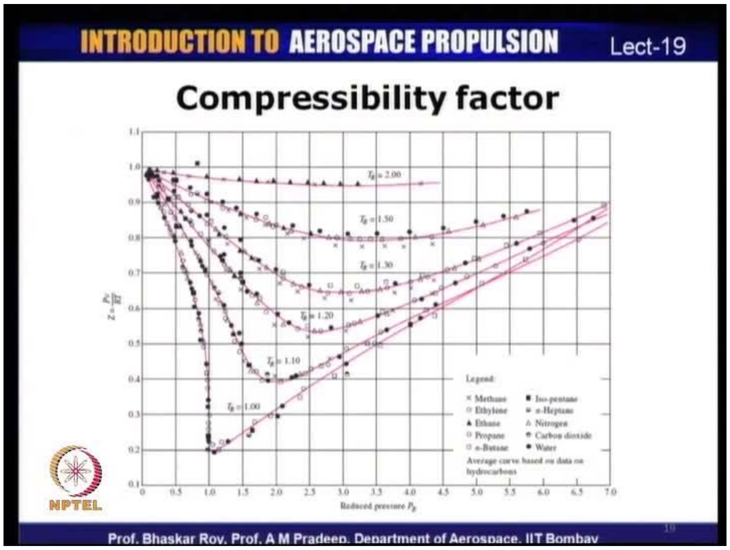

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Compressibility factor

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19

We can now express the compressibility factor in terms of reduced pressures and reduced temperatures for a variety of gases and then we can, what we get is the generalized compressibility chart. So, if you look at the generalized compressibility chart which are basically meant to be used for all set of gases, all gases and then we shall be able to make certain conclusions based on the generalized compressibility chart.

So, I have one example here of a compressibility chart which is plotted in terms of set of gases for methane, ethylene, ethane and so on under several gases which have been shown here on the y axis. We have the compressibility factor Z which is Pv by RT x axis is the reduced pressure and these graphs have been plotted for different reduced temperatures.

So, what we can see is temperature ratio, temperature, reduced temperature varying from 1 all the way up to 2 and so on. You will find in certain books these charts given for many more reduced temperatures all the way up to 5 or 6 and but the basic message is the same. That we shall discuss now. What you see here is that as the reduced pressures are lower, as it approaches 0, then the compressibility factor approaches 1; which means that as for very low pressures irrespective of what the temperature ratio is the compressibility factor approaches 1; which means all the gases will approach ideal gas behavior.

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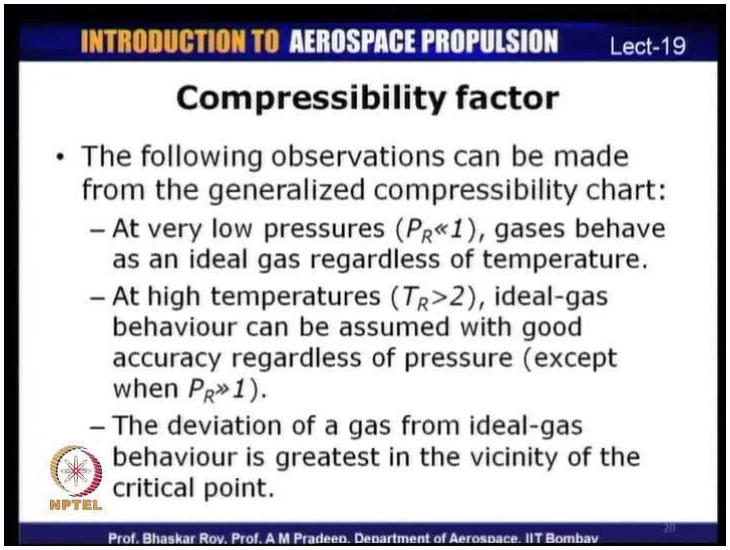

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Compressibility factor

- The following observations can be made from the generalized compressibility chart:
  - At very low pressures ($P_R \ll 1$), gases behave as an ideal gas regardless of temperature.
  - At high temperatures ($T_R > 2$), ideal-gas behaviour can be assumed with good accuracy regardless of pressure (except when $P_R \gg 1$).
  - The deviation of a gas from ideal-gas behaviour is greatest in the vicinity of the critical point.

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For certain reduced pressures you can say that you can see that the behavior and temperature ratios. The behavior is substantially different from that of ideal gas behavior. For example, for a reduced pressure of 1 and a reduced temperature of 1 the compressibility factor is 0.2 which means that it is substantially different from 1. It is substantially away from 1 which means that these, the gases at these reduced pressures and temperatures will deviate substantially from ideal gas behavior and so based on the general compressibility chart or generalized compressibility chart we can derive the following conclusions at very low pressures which we have seen where P R much less than 1 or is at as it approaches 1. Gas behavior is very similar to that of the ideal gas and regardless of temperature because all the temperature curves were merging towards Z equal to 1.

At high temperatures T R greater than 2 ideal gas behavior can be assumed regardless of the pressure which you can see here in this diagram. That for as you increase the reduced temperature at 2 or beyond that it is the curve is the more or less flat which means that regardless of pressure. The gas behavior is like that of an ideal gas which occurs for reduced temperatures of 2 and beyond that and the deviation of a gas from the ideal gas behavior is highest in the vicinity of the critical point. That is around critical point when let us say pressure reduced pressure is 1 and the reduced temperature is 1 that is at the critical point temperatures and pressures the deviation of the gas from the ideal gas behavior is the highest which also is seen clearly from this generalized compressibility chart.

So, these are some observations which we can derive when we look at the compressibility chart, that based on the compressibility chart you can actually see how an actual gas is with reference to an ideal gas in terms of the reduced temperatures and pressures. Finally, expressed in terms of the compressibility factor now what we had discussed, now was the equation of state as applied for an ideal gas.

Now, there are certain limitations as you we have already seen that it is only for a certain set of temperatures and pressure ranges that the behavior of a certain gas can be approximated; to that of an ideal gas; but, what about the other temperatures and temperature pressures? So, the ideal gas equation of state has lot of limitations and therefore, over the years there have been several other forms or modifications of the ideal gas equation of state which are meant to account for some of these deficiencies of the equation of state.

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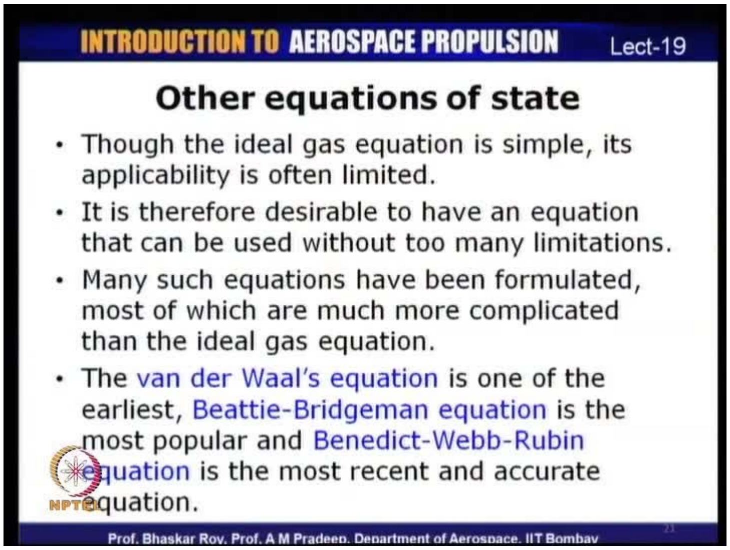

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Other equations of state

- Though the ideal gas equation is simple, its applicability is often limited.
- It is therefore desirable to have an equation that can be used without too many limitations.
- Many such equations have been formulated, most of which are much more complicated than the ideal gas equation.
- The van der Waal's equation is one of the earliest, Beattie-Bridgeman equation is the most popular and Benedict-Webb-Rubin equation is the most recent and accurate equation.

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21

So they have several equations which have been proposed. Some of them in fact, there are several of them. One of the earliest one is known as the Van der Waal's equation. It is the one of the earliest equation for a long time that was used. Then, the Beattie-Bridgeman equation is the one of the most popular equations and the one of the most recent and accurate equation is the Benedict-Webb-Rubin equation.

We will only discuss the only the first 2 equations little detail because, the third equation is very complicated and I would limit my discussion to the Van der Waal's equation and the Beattie-Bridgeman equation because these are the ones which have been used popularly.

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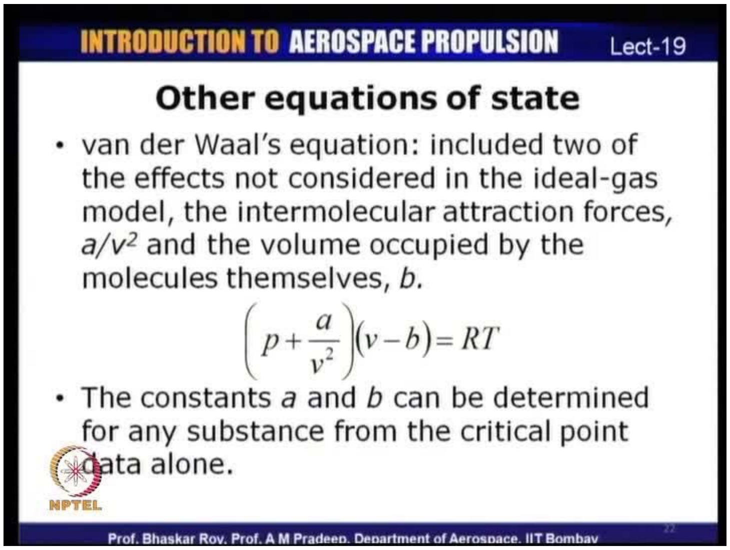

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Other equations of state

- van der Waal's equation: included two of the effects not considered in the ideal-gas model, the intermolecular attraction forces, a/v^2 and the volume occupied by the molecules themselves, *b*.

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

- The constants *a* and *b* can be determined for any substance from the critical point data alone.

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So, Van der Waal's equation basically includes the effect of intermolecular attractions which is expressed in terms of a by v squared, where a is a constant and also the volume occupied by the gas themselves. That is, there is a certain volume associated with the gas molecules. So, Van der Waal's equation takes in to account these 2 effects; one is the intermolecular attraction forces and also the volume of the gas. So, the Van der Waal's equation of state is p plus a by v square and v minus b where b is the volume of the molecules themselves; so that has been reduced from the volume itself.

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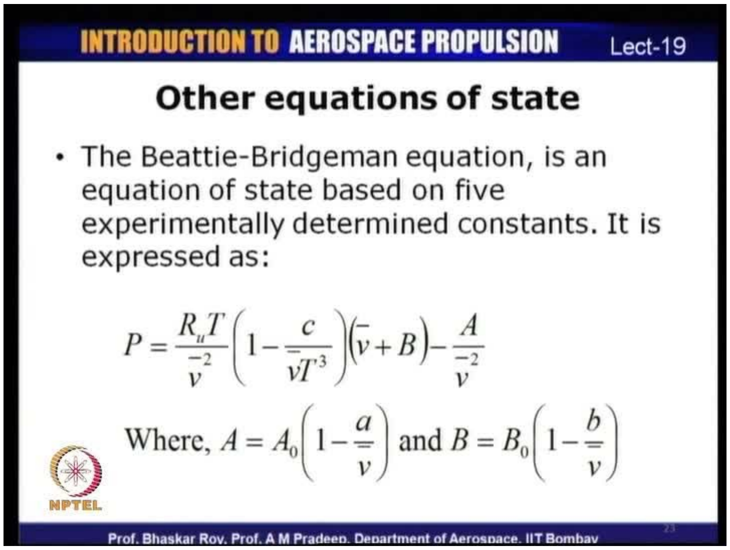

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Other equations of state

- The Beattie-Bridgeman equation, is an equation of state based on five experimentally determined constants. It is expressed as:

$$P=\frac{R_uT}{\bar{v}^2}\left(1-\frac{c}{\bar{v}T^3}\right)\left(\bar{v}+B\right)-\frac{A}{\bar{v}^2}$$

$$\text{Where, } A=A_0\left(1-\frac{a}{\bar{v}}\right) \text{ and } B=B_0\left(1-\frac{b}{\bar{v}}\right)$$

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So, p plus a by v square into v minus b is equal to RT. So, here these two constants need to be determined from the critical point data of that particular gas. So, this is the Van der Waal’s equation and the second equation which is more popularly used is the Beattie-Bridgeman equation and this is expressed in terms of 5 experimentally determined constants. It is basically, the equation is P is equal to R u T by v bar square into 1 minus c by v by v bar T cube multiplied by v bar plus B minus A by v bar squared where A and B are expressed again in terms of constants.

You can see that this equation is fairly quite complicated as compared to the simple ideal gas equation of state. However, this equation has been popularly used in getting much more better estimate of real gas behavior as compared to the ideal gas assumption.

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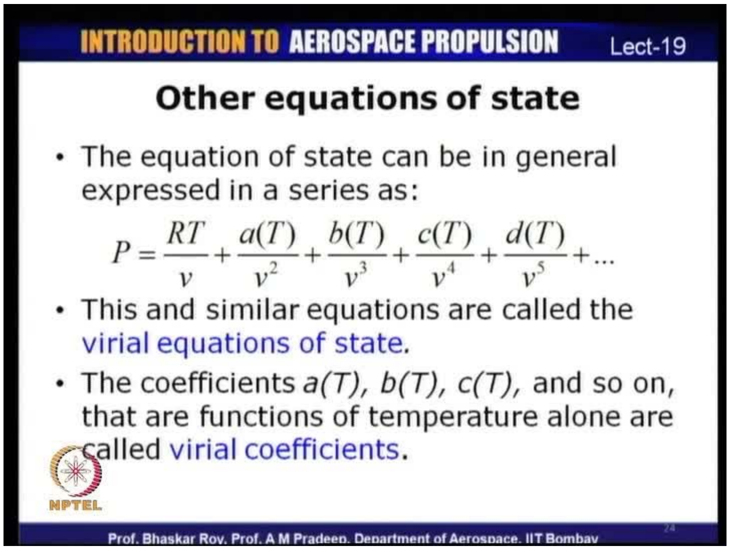

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Other equations of state

- The equation of state can be in general expressed in a series as:

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \dots$$

- This and similar equations are called the virial equations of state.
- The coefficients $a(T)$, $b(T)$, $c(T)$, and so on, that are functions of temperature alone are called virial coefficients.

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24

Basically, the equation of state can be expressed as a series. So, Pv is equal to RT can be also expressed as P is equal to RT by v plus a T by v square plus b T by v cube and so on. So, this is a series; it can basically be expressed as a series and so this and similar other equations are basically referred to as the virial equations of state.

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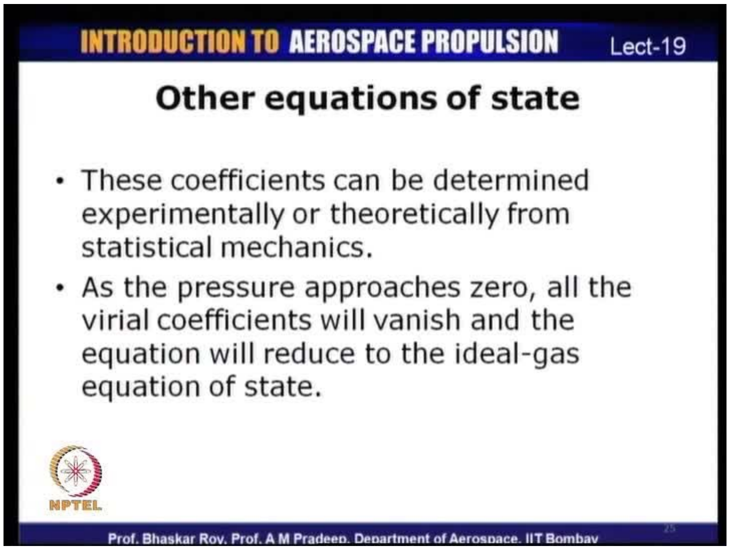

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

Other equations of state

- These coefficients can be determined experimentally or theoretically from statistical mechanics.
- As the pressure approaches zero, all the virial coefficients will vanish and the equation will reduce to the ideal-gas equation of state.

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These coefficients that you get here a of T b of T and so on, are simply functions of temperatures. These are referred to as the virial coefficients. So, there are other several sets of equations which are basically expressing the ideal gas equation in terms of a series and these are known as the virial equations of state.

So, these coefficients basically need to be determined either experimentally or theoretically from statistical mechanics and as the pressure approaches 0 you can see that virial coefficients will vanish and the equation will reduce to that of an a ideal gas equation of state. So, it is only accounting for as you deviate from the ideal gas behavior which could be at different higher pressures and so on. Then some of these equations will actually show up lot differences as compared to the ideal gas equation state and so similarly, in literature you would find there were, there are many more forms of the equation of state and many of them are very complicated and involve lot of other parameters and constants and coefficients which need to be determined experimentally.

Some of these are used in modeling of real gas effects especially, when they involve certain combustion of gases, etcetera. The combustion products no longer can be treated as an ideal gas and so you need set of equations which can model these effects in an accurate manner and it is in these applications that many of these equations are used. But, for simple thermodynamic analysis, it is always a practice to assume air or even the combustion products as an ideal gas and carry out analysis based on that assumption.

Now, we will now discuss another effect which is different from what we have already been discussing about. It is basically to do with flow passing through a constriction or a restricted passage or during a throttling process. Now, if you recall during our discussion on steady flow energy equation applied to such processes, we had derived that or we had understood that basically for throttling processes, the enthalpy remains a constant at that point. I also made a statement that during a throttling process, temperature may either be constant; it may increase or decrease and it depends upon a certain set of parameters.

So, we will now see what is it that causes a change in a temperature; it could either decrease or increase depending upon the pressure. So, we will now see how we can estimate or determine changes in temperature during a throttling process.

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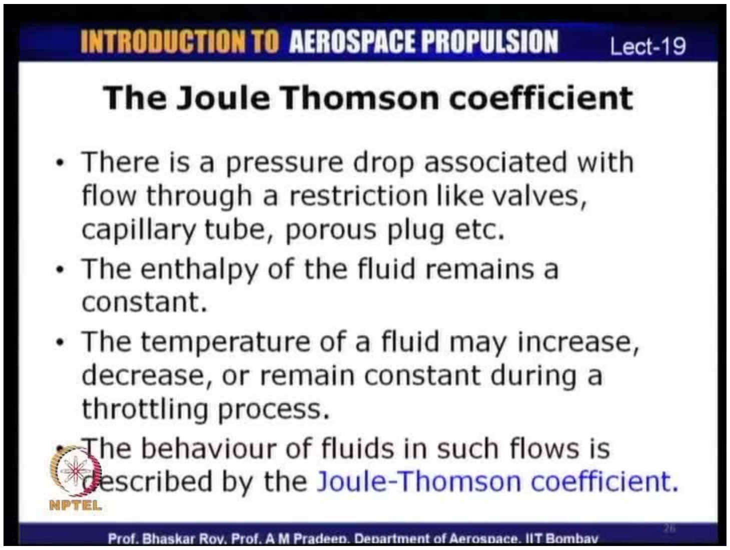

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The Joule Thomson coefficient

- There is a pressure drop associated with flow through a restriction like valves, capillary tube, porous plug etc.
- The enthalpy of the fluid remains a constant.
- The temperature of a fluid may increase, decrease, or remain constant during a throttling process.
- The behaviour of fluids in such flows is described by the Joule-Thomson coefficient.

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26

Now, during a throttling process there is definitely a pressure drop associated with flow when it passes through devices like valves or capillary tubes and so on. So, enthalpy of a fluid remains a constant which is basically an outcome of the energy equation. Now, the temperature may remain same; it may increase or it could decrease depending upon the throttling process.

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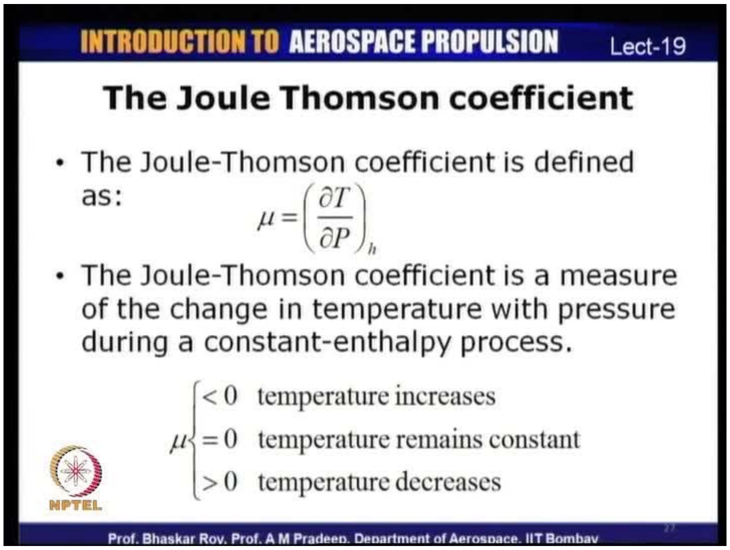

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The Joule Thomson coefficient

- The Joule-Thomson coefficient is defined as: $\mu = \left(\frac{\partial T}{\partial P}\right)_h$
- The Joule-Thomson coefficient is a measure of the change in temperature with pressure during a constant-enthalpy process.

$$\mu \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

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So the behavior of fluids during such flows is described by what is known as the Joule Thomson coefficient. So, let us what is meant by the Joules coefficient or joule Thomson coefficient. Joule Thomson coefficient mu is basically equal to partial derivative of temperature with pressure for constant enthalpy.

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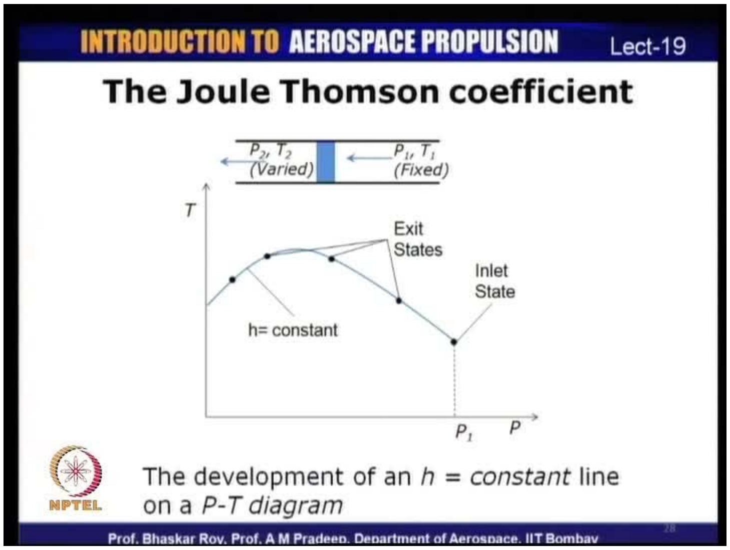

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The Joule Thomson coefficient

The development of an *h = constant* line on a *P-T diagram*

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So del T by del P at constant h is Joule Thomson coefficient. So, it follows from this that if mu is less than 0 the temperature will increase. If mu is equal to 0 temperature remains constant and if mu is greater than 0, the temperature decreases. So, if you could calculate this gradient of temperature with pressure during a constant enthalpy process, then depending upon the gradient you can determine whether temperature will increase remain constant or decrease.

So, let us look at one example here: we have flow passing through a porous plug here. The initial condition is P 1 and T 1 which is fixed and as you change the porosity, the downstream conditions can change; which means, if you start at the initial state here exit states which are shown by these black dots can be defined or can be varied depending upon the porosity here.

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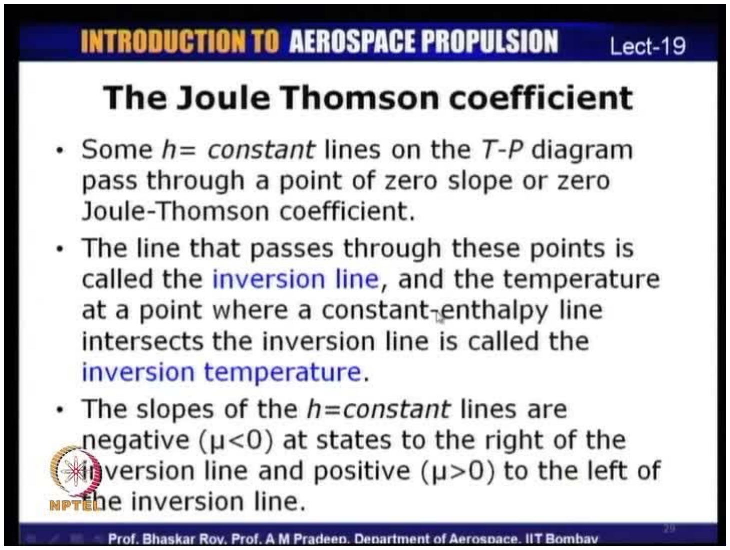

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The Joule Thomson coefficient

- Some *h= constant* lines on the *T-P* diagram pass through a point of zero slope or zero Joule-Thomson coefficient.
- The line that passes through these points is called the inversion line, and the temperature at a point where a constant-enthalpy line intersects the inversion line is called the inversion temperature.
- The slopes of the *h=constant* lines are negative (μ<0) at states to the right of the inversion line and positive (μ>0) to the left of the inversion line.

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So, you may end up getting different exit states on the constant enthalpy line. Now, it means that there is certain point on the enthalpy equal to constant line where this slope is 0 or where you have Joule Thomson coefficient equal to 0. So, the line that passes through all these 3 points is known as the inversion line and the temperature at a point where a constant enthalpy line intersects the inversion line is called the inversion temperature.

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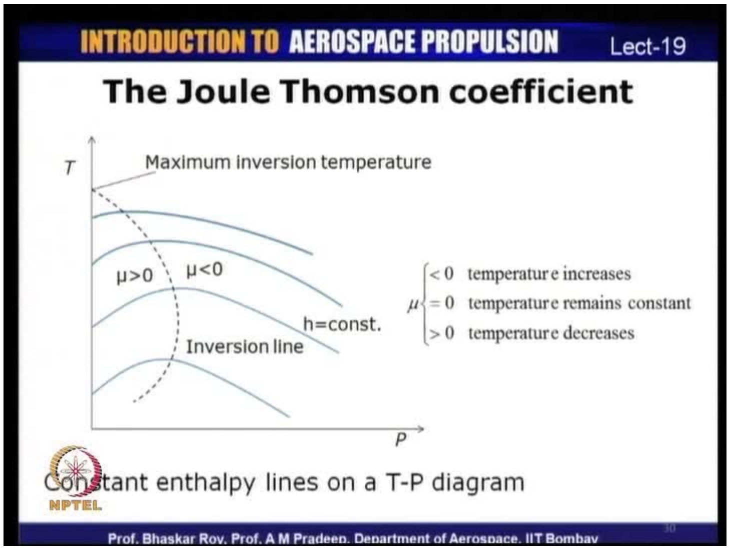

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

The Joule Thomson coefficient

$$\mu \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

Constant enthalpy lines on a T-P diagram

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30

The slopes of h equal to constant line are negative at states to the right of the inversion line and positive to the left of the inversion line. So, that will be clear from this sketch. I have shown here illustratively that on this constant enthalpy lines plotted on the temperature pressure plot, all these lines are enthalpy equal to constant. So, at the point where slope is equal to 0 if you join all those points you get the inversion line and this temperature is known as the inversion temperature.

So on left of this inversion line you have mu is equal mu is greater than 0 which means temperature decreases in this zone and if you are operating in the other zone where mu is less than 0, the temperature should increase which means that as you start throttling from here. If you are operating on the positive slope line then you end up getting reduced temperature and if you end up operating on the right hand side of the inversion line the temperature after the throttling process will increase.

On a constant enthalpy line it is necessary. If your aim is to reduce temperature then it is necessary that you operate on the right hand side where the pose slope is positive and if you are operating on the right hand side you end up with getting an increase in temperature. So, this is basically the significance of the Joule Thomson effect or Joule Thomson coefficient which basically helps us in understanding that as you throttle. It is not necessary that temperature will always decrease because throttling devices are very commonly used in refrigeration cycles and air conditioning systems and so on. And, so if you need throttling to be effective you need to make sure that on the constant enthalpy line you are operating towards the left of the inversion line where the Joule Thomson coefficient is greater than 0 which means that you will end up getting a reduced temperature. But, if you are operating on the right hand side the temperature will increase so that that was about the Joule Thomson coefficient which describes throttling process in much more detail. So, let us recap what we had discussed in today’s lecture we are coming towards the end of this lecture.

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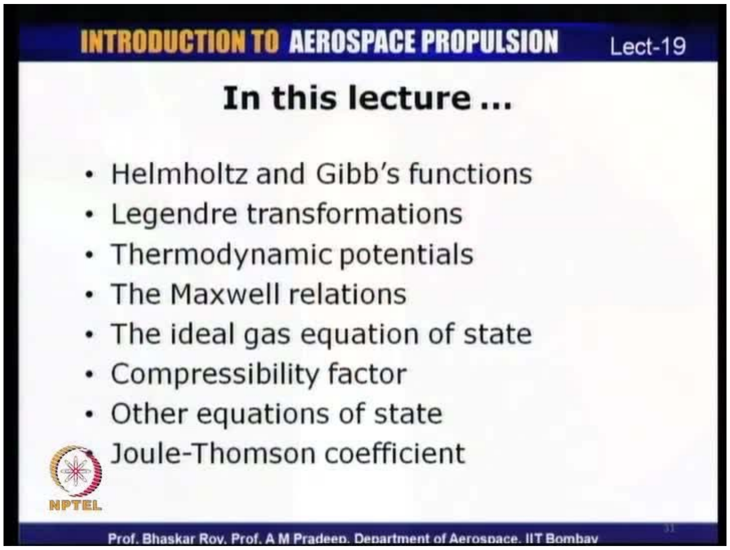

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

In this lecture ...

- Helmholtz and Gibb’s functions
- Legendre transformations
- Thermodynamic potentials
- The Maxwell relations
- The ideal gas equation of state
- Compressibility factor
- Other equations of state
- Joule-Thomson coefficient

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In today’s lecture we had discussed about 2 new functions the Helmholtz and the Gibbs process which are combination properties like enthalpy we had discussed about Legendre transformations which help us in mapping set of parameters to another set of parameters then as a consequence of Legendre transformations we discussed about thermodynamic potentials and then the Maxwell relations which form the basic tool for analysis different thermodynamic systems.

We discussed about the ideal gas equation of state and the real gas effects and how to account for real gas effects in term of the compressibility factor and also we discussed about the other equations of state like the Van der Waal’s equation and so on.

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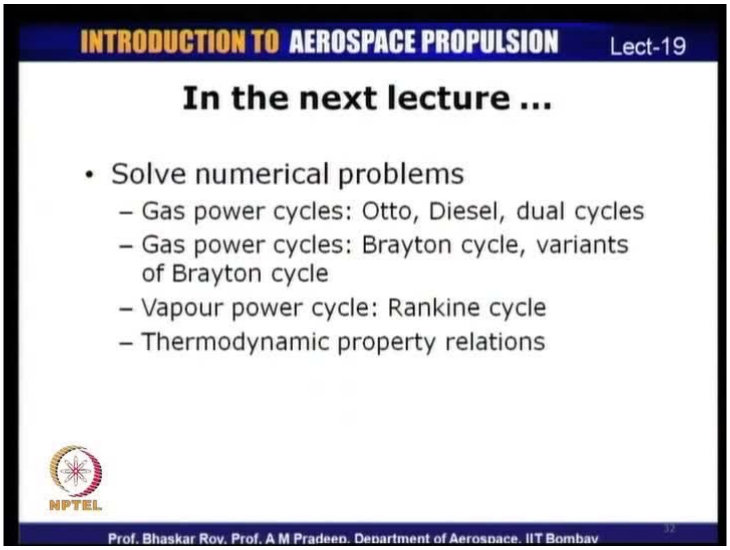

INTRODUCTION TO AEROSPACE PROPULSION Lect-19

In the next lecture ...

- Solve numerical problems
  - Gas power cycles: Otto, Diesel, dual cycles
  - Gas power cycles: Brayton cycle, variants of Brayton cycle
  - Vapour power cycle: Rankine cycle
  - Thermodynamic property relations

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Subsequently, we discussed about the Joule Thomson coefficient which is basically applicable for throttling processes. So that brings us to the end of this lecture and in the next lecture what we shall do is we will have a tutorial session we shall be solving numerical problems related to gas power cycles from Otto diesel and dual cycles.

We are will also be solving some problems from Brayton cycle and variants of Brayton cycle; like Brayton cycle with regeneration reheating and so on and then we will be discussing about the vapor power cycle. Basically, the Rankine cycle and possibly we will also solve some problems based on today’s lecture; that is the thermodynamic property relation. So, we will shall take up these during the next lecture which would be lecture 20.