



Introduction to Aerospace Propulsion

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Lecture No - 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

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:

$$a = u - Ts$$

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.

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,

$$da = du - Tds - sdT$$

$$dg = dh - Tds - sdT$$

Legendre transformations

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

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

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

Alternatively, in the entropy representation,

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

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

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.

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

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

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

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

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.

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, $h = u + Pv$

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.

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.

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.

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.

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.

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.

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,

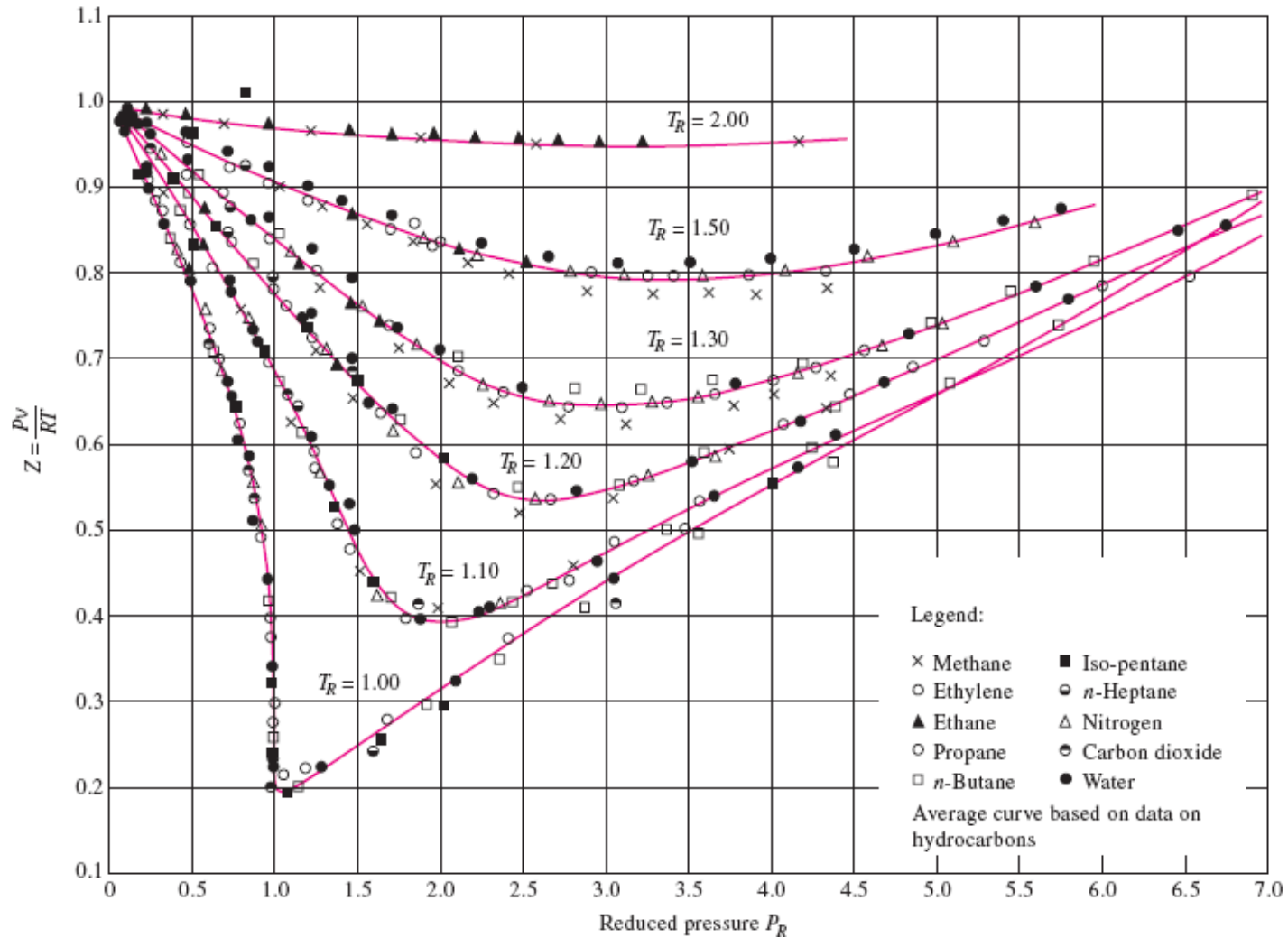
$$P_R = P/P_{cr} \quad \text{and} \quad T_R = T/T_{cr}$$

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

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.

Compressibility factor



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.

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.

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.

Other equations of state

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

$$P = \frac{R_u T}{v} \left(1 - \frac{c}{vT^3} \right) \left(\frac{v}{v_0} + B \right) - \frac{A}{v}$$

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

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**.

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.

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**.

The Joule Thomson coefficient

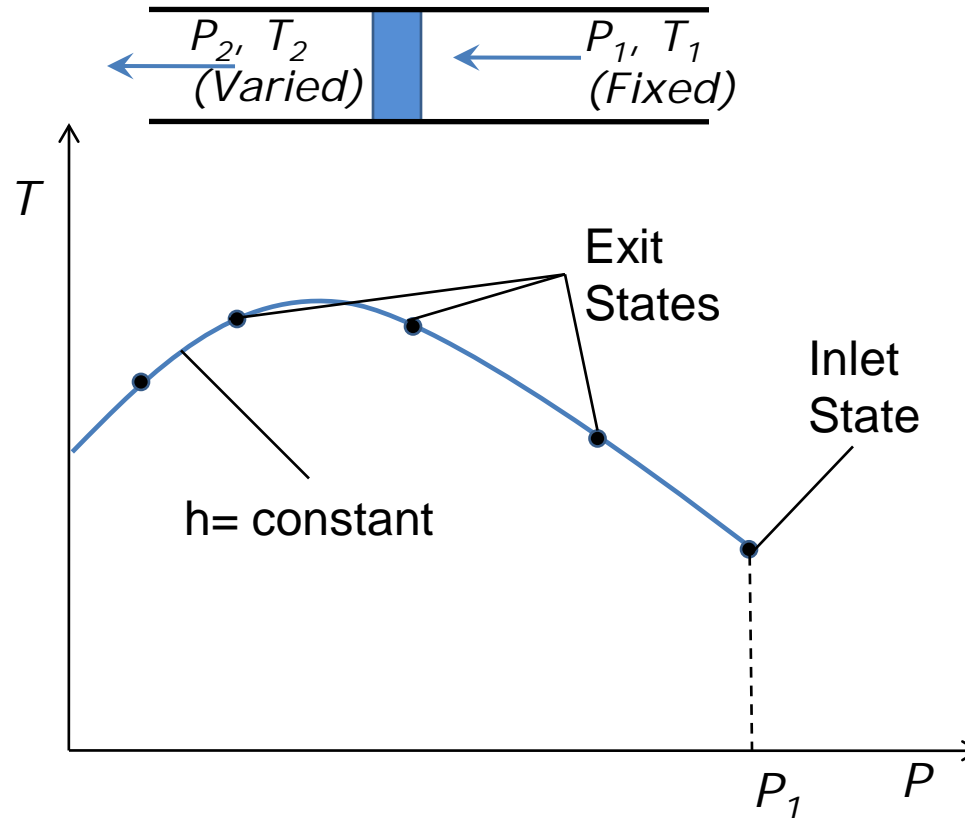
- The Joule-Thomson coefficient is defined as:

$$\mu = \left(\frac{\partial T}{\partial P} \right)_h$$

- The Joule-Thomson coefficient is a measure of the change in temperature with pressure during a constant-enthalpy process.

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

The Joule Thomson coefficient

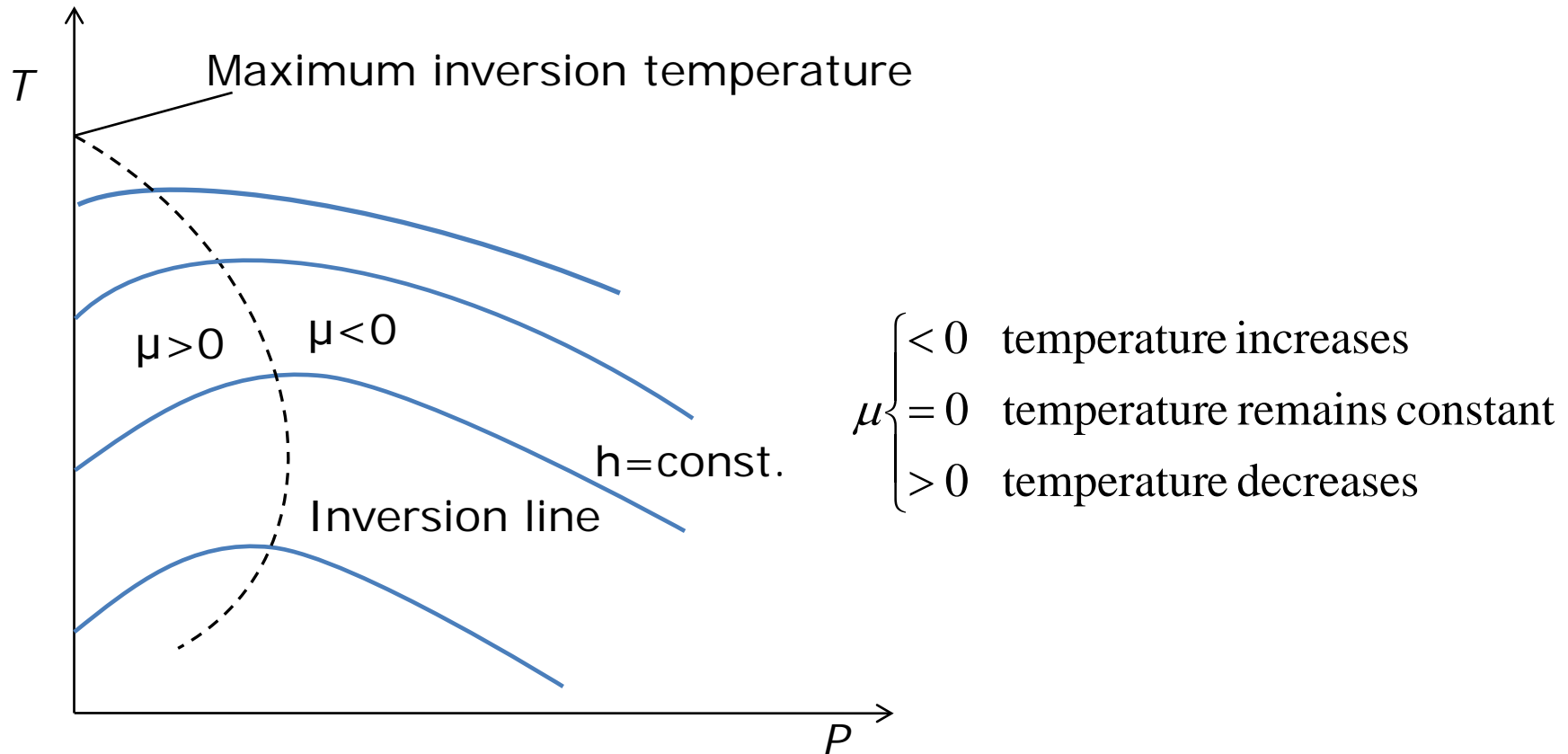


The development of an $h = \text{constant}$ line on a $P-T$ diagram

The Joule Thomson coefficient

- Some $h = \text{constant}$ 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 $h = \text{constant}$ lines are negative ($\mu < 0$) at states to the right of the inversion line and positive ($\mu > 0$) to the left of the inversion line.

The Joule Thomson coefficient



Constant enthalpy lines on a T-P diagram

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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