

- Recap: Lecture 19: 3rd March 2014, 1130-1230 hrs.
 - Exergy change of a system
 - Exergy and exergy change of a closed system
 - Exergy and exergy change for a flow process
 - Decrease of exergy principle
 - Exergy destruction
 - Exergy balance

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,

$$da = du - Tds - sdT$$

$$dg = dh - Tds - sdT$$

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 Gibbs'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,

$$\begin{aligned}\left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial P}{\partial s}\right)_v \\ \left(\frac{\partial T}{\partial P}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_P \\ \left(\frac{\partial s}{\partial v}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_v \\ \left(\frac{\partial s}{\partial P}\right)_T &= -\left(\frac{\partial v}{\partial T}\right)_P\end{aligned}$$

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,

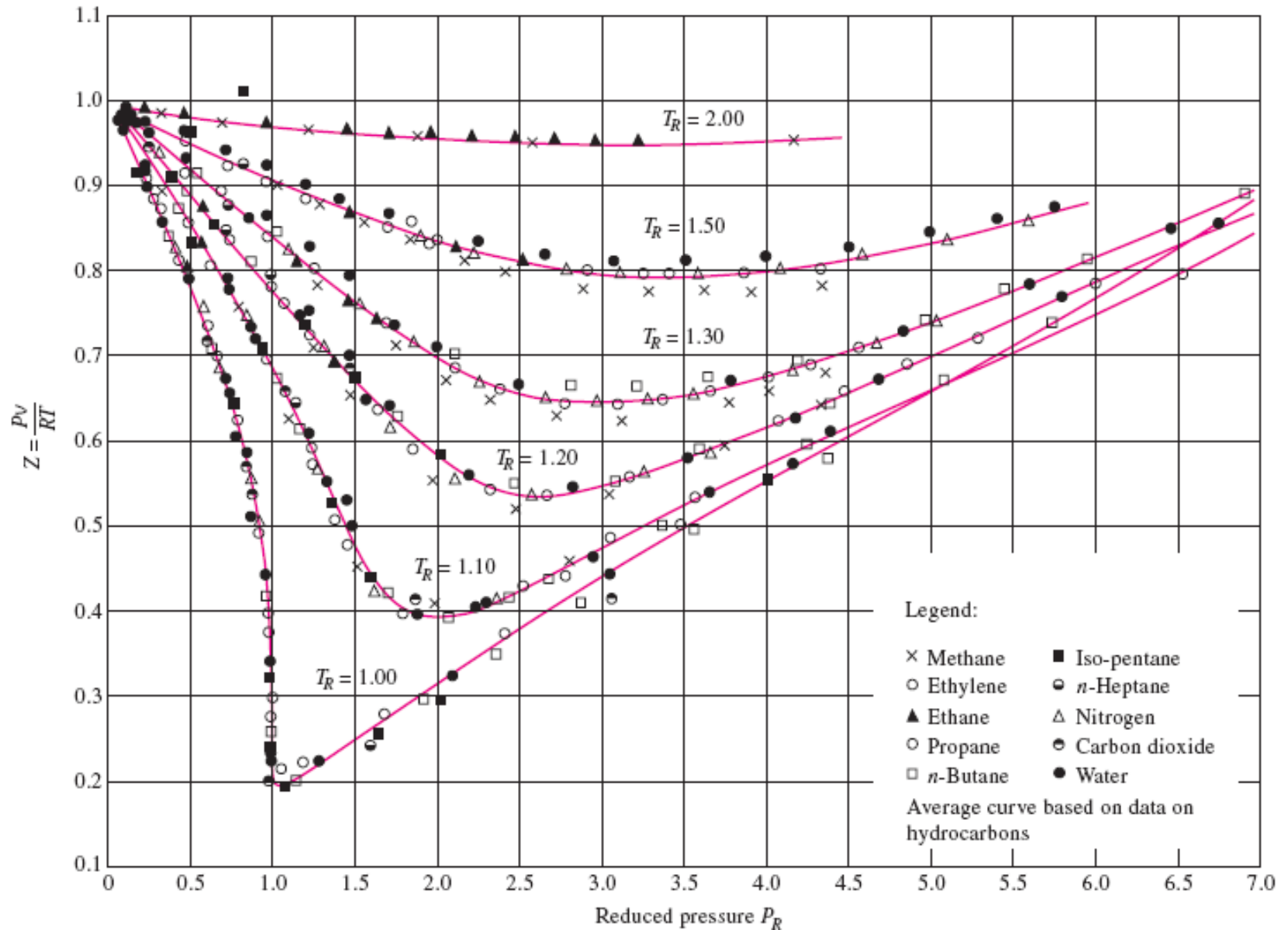
$$PR = P/P_{cr} \quad \text{and} \quad TR = T/T_{cr}$$

where, PR is the reduced pressure and TR 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 ($PR \ll 1$), gases behave as an ideal gas regardless of temperature.
 - At high temperatures ($TR > 2$), ideal-gas behaviour can be assumed with good accuracy regardless of pressure (except when $PR \gg 1$).
 - 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.

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

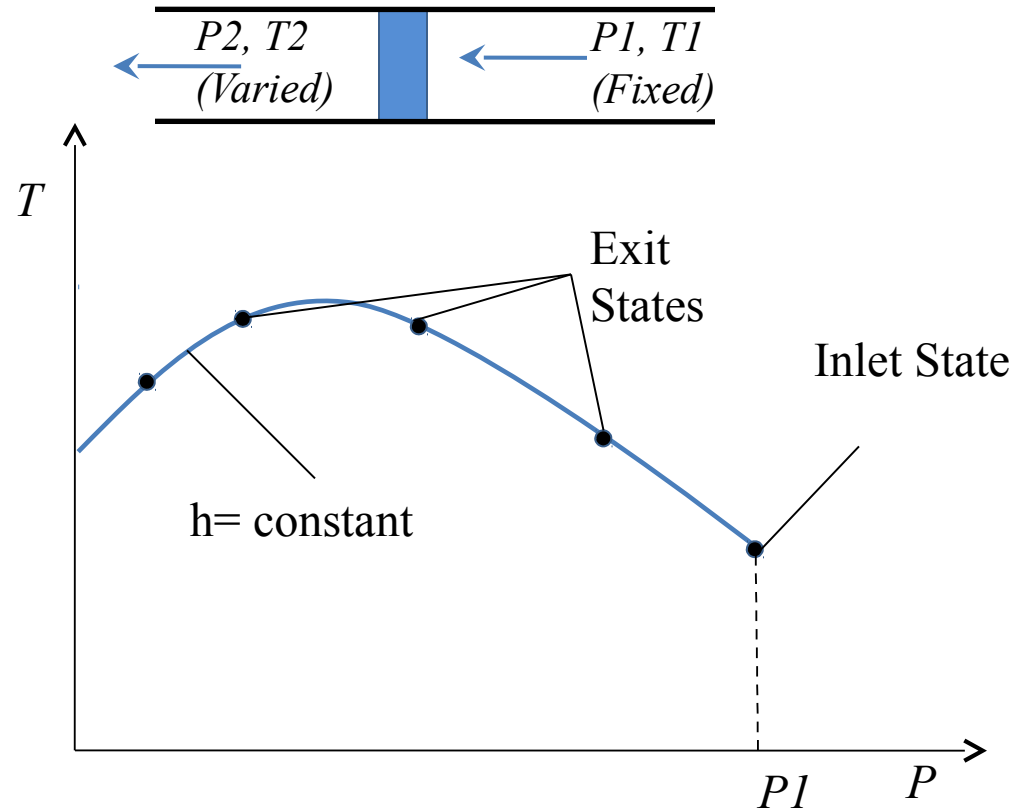
- The Joule-Thomson coefficient is defined as:

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

- 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

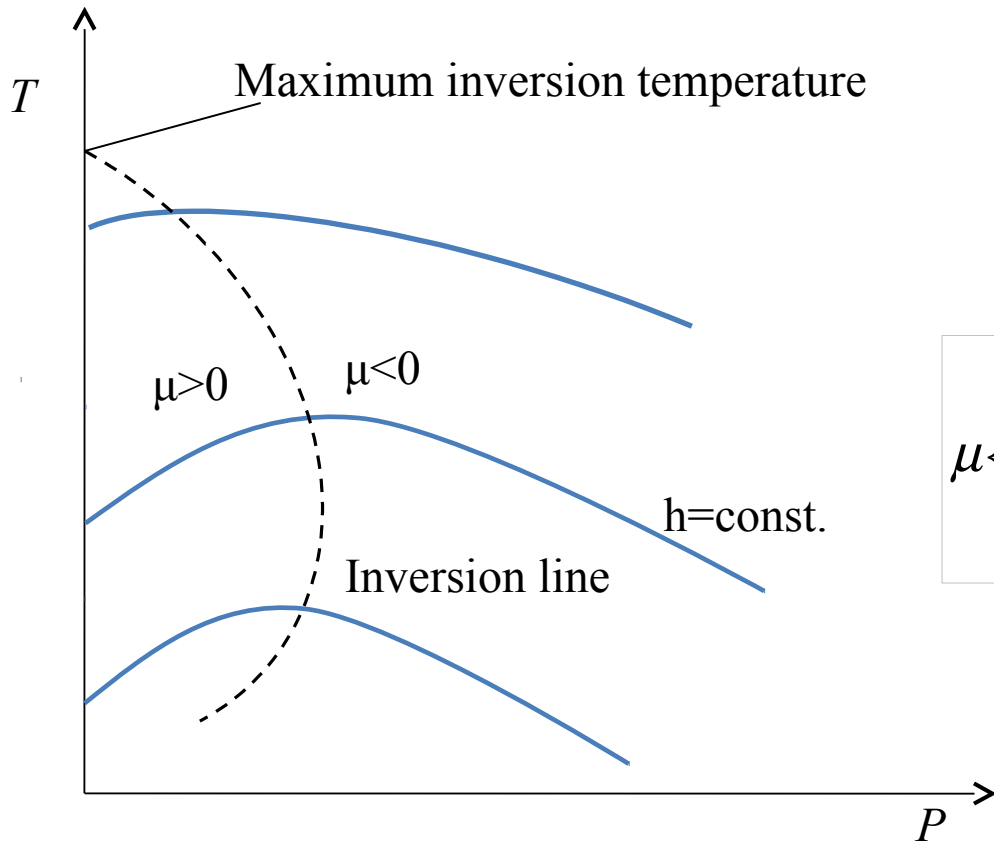


The development of an $h = \text{constant}$ line on a P - T diagram

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



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

Constant enthalpy lines on a T-P diagram