Hydrogen Energy: Production, Storage, Transportation and Safety

Prof. Pratibha Sharma
Department of Energy Science and Engineering
Indian Institute of Technology, Bombay

Lecture - 33

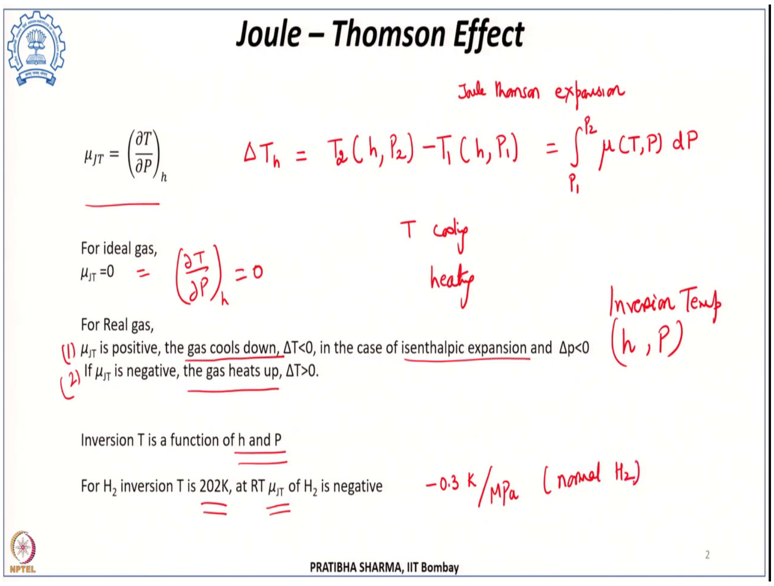
Fundamentals of Hydrogen Compression and Expansion

In the previous class we have studied underground hydrogen storage. Underground hydrogen storage is meant for large scale storage; it can provide grid stability it can assure like the seasonal storage. And the capacities, which usually we consider when we look at the underground hydrogen storage is above 5 gigawatt hour.

It can also provide discharge or withdrawal of hydrogen for several days; however, if the requirement is a small scale hydrogen storage for stationary or portable applications for vehicular applications. In that case like whether the storage is required for daily storage or in onboard tanks in that case hydrogen can be stored in the compressed state or it can be stored in liquid state.

Now what typical technology will be used for hydrogen storage that is decided based on the end use application, the boundary conditions the requirements of the end use applications. So, today we will start up the hydrogen compression and expansion we will first look at some of the fundamentals, thermodynamics of hydrogen compression and expansion process. These concepts you would have earlier studied in your previous classes and we are just going to revise those concepts to start with let us first look at the Joule Thomson effect.

(Refer Slide Time: 01:48)



Joule – Thomson Effect

Joule Thomson expansion

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

$\Delta T_h = T_2(h, P_2) - T_1(h, P_1) = \int_{P_1}^{P_2} \mu(T,P)\, dP$

For ideal gas,
$\mu_{JT} = 0$ $= \left(\frac{\partial T}{\partial P}\right)_h = 0$

T cooling

heating

For Real gas,
(1) μ_{JT} is positive, the gas cools down, $\Delta T<0$, in the case of isenthalpic expansion and $\Delta p<0$
(2) If μ_{JT} is negative, the gas heats up, $\Delta T>0$.

Inversion Temp
(h, P)

Inversion T is a function of h and P

For H_2 inversion T is 202K, at RT μ_{JT} of H_2 is negative

-0.3 K/MPa (normal H_2)

PRATIBHA SHARMA, IIT Bombay

Now, when there is an adiabatic throttling at a constant enthalpy through an insulated porous plug, then the expansion is known as Joule Thomson expansion. Now, depending upon whether the temperature of the fluid or gas it increases decreases or stays constant the effect is known as Joule Thomson effect. And the Joule Thomson coefficient it is given by the change in temperature with the change in pressure at a constant enthalpy.

We can also find out the temperature change at a constant enthalpy as the temperature T2 at enthalpy h when the pressure is P2 the final pressure is P2 minus the temperature T1 the initial temperature enthalpy constant and the initial pressure. Now, this can also be obtained as integrating over say pressure P1 to P2 the Joule Thomson coefficient which is a function of temperature and pressure times dP.

Now if we consider ideal gas case then during an isenthalpic process there is no change in temperature of the gas. So, for an ideal gas the del T upon del P at constant enthalpy this Joule Thomson coefficient remains 0. However, when we consider a real gas in contrast to the ideal gas where, there is an attractive interaction or a repulsive interaction that acts between the molecules of the gas.

The change in temperature occurs when there is a change in pressure. Now depending upon how the gas molecules interact if they interact attractively, in that case the if there is an expansion; that means, the pressure if it reduces or the volume increases in that case the potential energy increases. Now, to keep the internal energy constant the kinetic energy of the gas decreases and thus the temperature also reduces. So, if it is attractive interaction then it could result into cooling of the gas.

However, if the molecules of the gas it interacts repulsively in that case when there is an expansion pressure decreasing volume increasing, then the potential energy of the gas it decreases. To keep the internal energy constant, the kinetic energy of the gas or the temperature of the gas increases. And in that case we can observe heating inside the gas heating in the gas. Now there is a temperature, which is known as inversion temperature this inversion temperature it depends upon enthalpy and pressure.

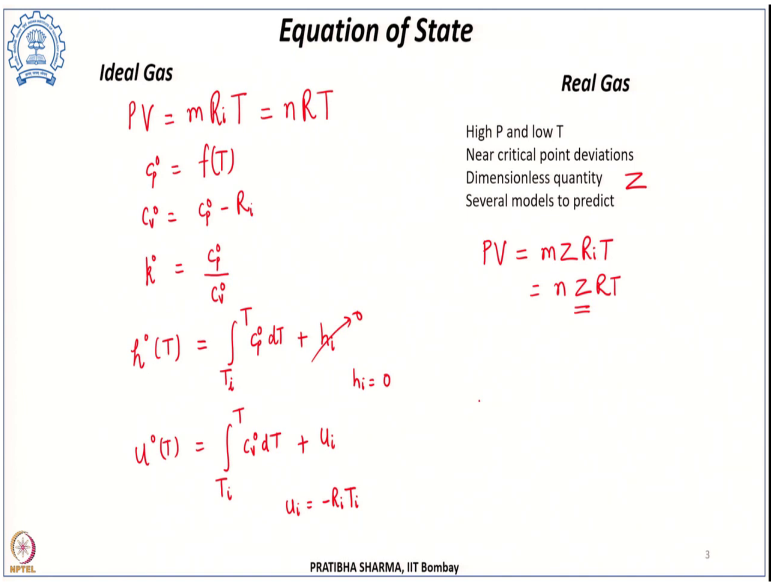
So, this is a function of enthalpy and pressure now depending upon the thermodynamic state which thermodynamic state it is, we can have Joule Thomson coefficient either positive or negative. Like if we consider one of the thermodynamic state where, the Joule Thomson coefficient is positive. That means if there is a pressure decrease on expansion, there is a positive change in the Joule Thomson coefficient. That means, if the pressure decreases in that case the temperature also decreases.

So, on expansion there is a cooling effect which is being observed or the gas cools down in case of an isenthalpic expansion process. There could be another thermodynamic state where the Joule Thomson coefficient is negative. That means, if there is a decrease in pressure because of the expansion the temperature increases; that means, the gas gets heated up. So, in the expansion of the gas it the temperature of the gas increases. Now this inversion temperature depends on enthalpy and pressure, for hydrogen this inversion temperature is 202 kelvin.

That means, if we want to cool down the hydrogen to liquefy it during the liquefaction process using a Joule Thomson valve or a throttle valve. In that case we have to reduce the temperature of hydrogen below 202 kelvin else there will be a negative Joule Thomson effect observed. At room temperature the Joule Thomson coefficient this is negative for hydrogen, it has a value of minus 0.3 kelvin per mega pascal for hydrogen this is for normal hydrogen.

Now, the another thing let us revise is the equation of state. There are different independent state variables, which are related and can be expressed in terms of equation of state. This equation of state is essential or it is the fundamental in providing or describing the information about the nature of the gas, how it is going to behave.

(Refer Slide Time: 07:25)



Equation of State

Ideal Gas

$PV = mR_iT = nRT$

$c_p^o = f(T)$

$c_v^o = c_p^o - R_i$

$k^o = \frac{c_p^o}{c_v^o}$

$h^o(T) = \int_{T_i}^{T} c_p^o \, dT + \cancel{h_i}^{\,0}$

$h_i = 0$

$u^o(T) = \int_{T_i}^{T} c_v^o \, dT + u_i$

$u_i = -R_iT_i$

Real Gas

High P and low T

Near critical point deviations

Dimensionless quantity Z

Several models to predict

$PV = mZR_iT$

$= n\underline{\underline{Z}}RT$

PRATIBHA SHARMA, IIT Bombay

For example, if we consider an ideal gas we know the ideal gas law where the pressure volume and temperature are related as it is mR_iT, where m is mass, R_i is the specific gas constant T is temperature, P is pressure and v is volume or we can also write it as molar mass times the universal gas constant and temperature. We can also write the isobaric specific heat for an ideal gas this is a function of temperature.

This is the isobaric specific heat; the isochoric specific heat we can write it as isobaric specific heat minus the gas constant. We can define for an ideal gas an isentropic exponent, which is the ratio of isobaric specific heat to the isochoric specific heat. At the same time, we can find out the enthalpy of the gas for an ideal gas the enthalpy. We can find out by integrating from some reference temperature let us say it is T_i to a final temperature T we can integrate the isobaric specific heat with temperature.

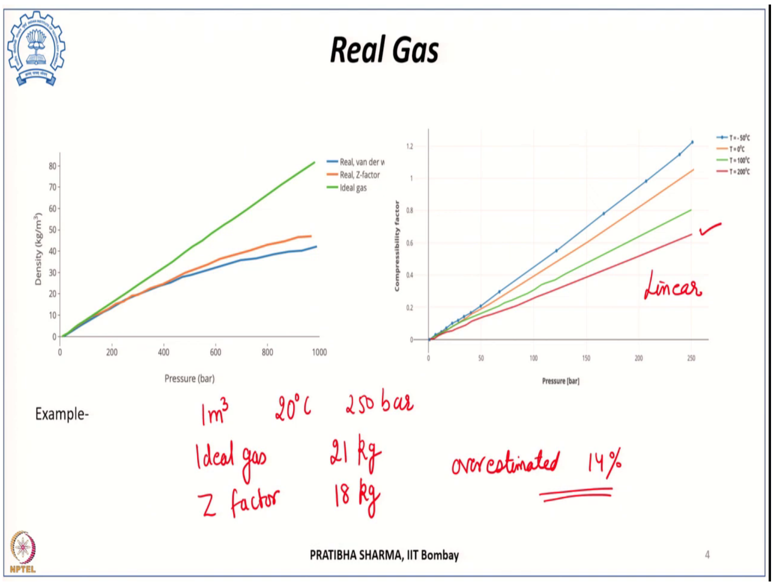
And then we can have some initial enthalpy and considering that enthalpy initial enthalpy to be 0, this term can become 0. For an ideal gas we can also find out the internal energy, again some reference temperature integrated between the limits of that reference temperature and temperature T the isochoric specific heat and some reference value of that specific internal energy now this reference specific internal energy is given by the gas constant and that initial temperature.

Considering ideal gas, we are able to explain many of the phenomena many of the cases and we can still explain those with very good accuracy. But when it comes to considering high pressure or low temperature case, in that case there is a deviation from the ideal gas behavior and if we still use the ideal gas equation of state then we may result we may end up in getting erroneous results or deviations.

Now it is observed that as we move towards the critical point these deviations increase or the change in the deviations is higher when we approach the critical point. Now in order to account for this deviation of a real gas from an ideal gas, we can include a dimensionless quantity, which is known as the compressibility factor. Now if we include that compressibility factor in the equation of state then we can rewrite the equation of state for real gas as PV is equal to mZR_iT or it can be nZRT.

So, this compressibility factor it is also not constant it also depends upon the temperature and pressure. Now to know the behavior of real gases there are several models which are there existing in the literature which can predict the behavior of the real gas. Now, this compressibility factor the dimensionless quantity, which tells us the difference or the deviation between the real and ideal gas behavior.

(Refer Slide Time: 11:19)



Real Gas

Example- $1 m^3$ 20°C 250 bar

Ideal gas 21 kg overestimated 14%

Z factor 18 kg

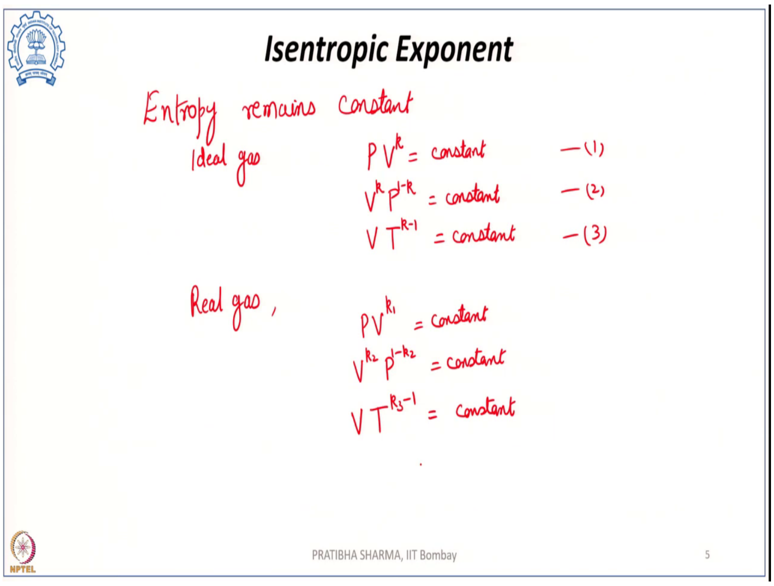
PRATIBHA SHARMA, IIT Bombay

That itself changes with temperature and pressure, so it is changing with temperature and pressure. For a constant temperature if we plot the compressibility factor, in that case we can see that it is showing a linear behavior at a particular temperature. Now as the temperature increases, so this is a higher temperature the slope is found to decrease for the variation of compressibility factor with the pressure. Now this is what is representing the how accurate will be if we consider the ideal gas behavior or under what conditions we need to consider the real gas behavior.

For example, if we consider a storage tank let us say having a geometric volume of 1 meter cube and the temperature condition is say 20 degree centigrade and we have compressed the gas at 250 bar. Now, if we use the ideal gas equation to find out the mass stored and if we use the compressibility factor.

In that case we find that using the compressibility factor the mass stored comes out to be 18 kg while, considering the ideal gas behavior it comes out to be 21 kg. So that means, if we consider the ideal gas behavior then we have overestimated the mass of hydrogen stored in that storage vessel by about 14 percent. And that tells us that under conditions of higher pressures we need to consider the real gas equation of state.

(Refer Slide Time: 13:07)



Isentropic Exponent

Entropy remains constant

Ideal gas

$PV^k = \text{constant}$ — (1)

$V^k P^{1-k} = \text{constant}$ — (2)

$V T^{k-1} = \text{constant}$ — (3)

Real gas ,

$PV^{k_1} = \text{constant}$

$V^{k_2} P^{1-k_2} = \text{constant}$

$V T^{k_3-1} = \text{constant}$

PRATIBHA SHARMA, IIT Bombay

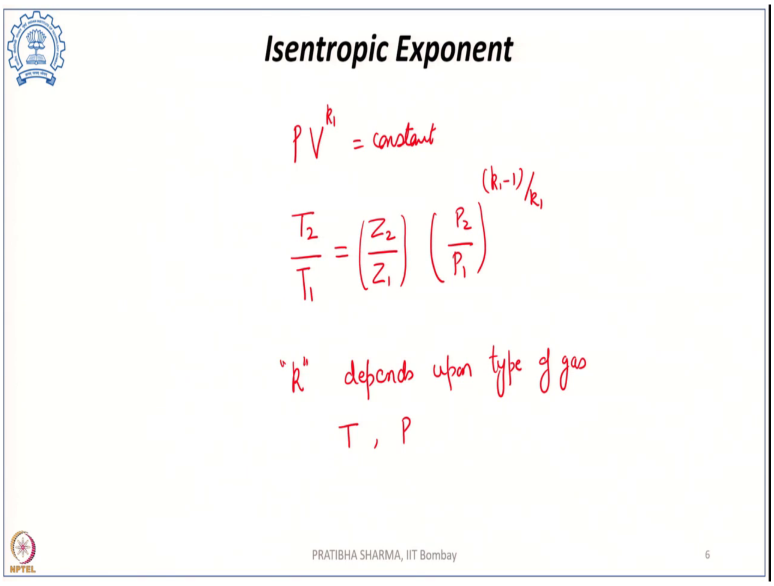
Now, there are different real gas equations of state available in the literature that can be used to find out the compression as well as expansion work, which will be required that we will see. If we consider a process which is isentropic; that means, the entropy of the system remains constant. Now here we need to consider an isentropic exponent, which along with the different state variables.

The independent state variables we can have different equations of state with the different independent variables considering the entropic isentropic exponent. And then using that we can describe the different processes. We can understand better the compression and expansion of the different gases.

Now if we consider like the independent variable as pressure and volume in that case, the exponent is k. So, PV^k this is constant this is one of the equation, which relates pressure and volume. If we consider this for an ideal gas then the exponent remains almost constant we can relate with volume and pressure, such that V^kP^{1-k} this is constant. We can also relate the volume and temperature. So, for ideal gas the relationship between the state variables the pressure volume and temperature and isentropic exponent is given by these expressions.

However, if we consider the case of a real gas in that case, the exponent which is used for different state variables for different equation each of these equation that exponent also differs. So, in case of a real gas we can write the expression as $1\text{-}k_2$ is equal to constant. So, it for the first equation we have used k1, for the second equation we have used k2 and for the third equation k3. So, these exponents differ depending upon which state variables these are connecting and these exponent this exponent also changes with temperature and pressure.

(Refer Slide Time: 16:09)



Isentropic Exponent

PV^{k_1} = constant

$$\frac{T_2}{T_1} = \left(\frac{Z_2}{Z_1}\right)\left(\frac{P_2}{P_1}\right)^{(k_1-1)/k_1}$$

"k" depends upon type of gas

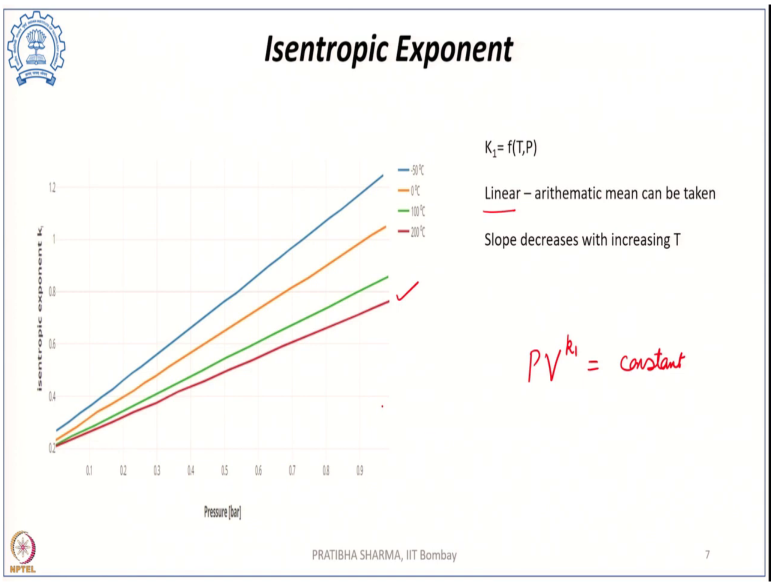
T , P

PRATIBHA SHARMA, IIT Bombay

Now, if we want to find out the final temperature using these exponent in that case we can consider let us for example, let us consider the first equation which was PV^{k1}= constant. So, if on compression we want to find the final temperature T2 then that is related to the initial temperature T1 by the ratio of the compressibility factor Z2 upon Z1 pressure ratio P2 upon P1 raised to power k1-1 over k1.

So, this exponent k it depends upon the nature of the gas, which type of gas we are considering and what is the temperature and pressure. So, it behaves differently at different temperatures and pressure.

(Refer Slide Time: 17:23)



Isentropic Exponent

$K_1 = f(T,P)$

Linear – arithematic mean can be taken

Slope decreases with increasing T

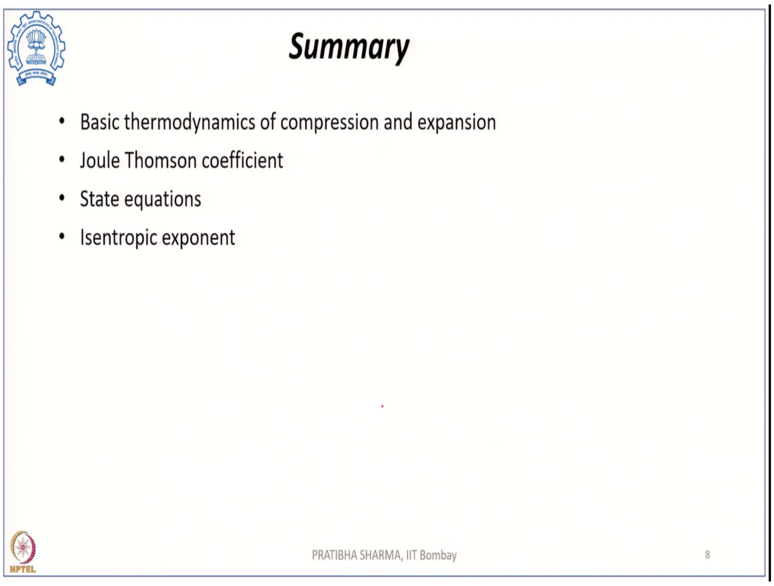
PV^{k_1} = constant

PRATIBHA SHARMA, IIT Bombay

Now, this is the variation for the isentropic coefficient k1, which we have used for the state equation relating pressure and volume. So, the k1 exponent if we see how it varies with different pressure at different temperature, we can see that there is a linear variation. Now we will study the work of compression in that case we will see that the isentropic exponent could have a different value at different states.

Now, when we consider the variation to be linear the process the calculation becomes simpler and we can have take the arithmetic mean in the two different states to find out the exponent at a particular state. Also we can see that as the temperature increases, so this is the highest temperature for this graph the slope also decreases for the isentropic exponent.

(Refer Slide Time: 18:33)



Summary

- Basic thermodynamics of compression and expansion
- Joule Thomson coefficient
- State equations
- Isentropic exponent

PRATIBHA SHARMA, IIT Bombay

To summarize this part, we have seen the basic thermodynamics of the compression and expansion process. The various state equations that we will be using for finding out the work of compression and explaining the hydrogen compression in more detail; we have seen the Joule Thomson coefficient the different state equations, what is the isentropic exponent and how is it related to the different state variables in this class.

In the next class we will calculate the work of compression, which is required for a compressed hydrogen storage.

Thank you.