

Chemical Engineering Thermodynamics
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Lecture – 05
The Ideal Gas

Hello and welcome back to this course on Chemical Engineering Thermodynamics. I hope you have been enjoying the course so far. In the last lecture we looked at several applications of the first law of thermodynamics for both open and closed systems. How we calculate heat, work, internal energy changes given some of the other, some of these variables, we try to find the other variables.

If you recall one of the things we have done during these calculations is, taking either the change in internal energy to be $C_v \Delta T$ or change in enthalpy to be $C_p \Delta T$. And then values of C_p and C_v were assumed to be constant with temperature. So, we use the things such as C_p is $\frac{7}{2} R$ or C_v is $\frac{5}{2}$ times the gas constant.

Those were approximations, they help us in understanding the concepts early on when we apply the first law. But then in real life these in the these C_p and C_v the specific heats are essentially derivatives of enthalpy and internal energy. And since for a single phase system containing one chemical species, we already discussed that enthalpy and internal energy or any thermal these variables depend on two intensive variables, right.

We need two intensive variables to fix the state of the system showing include; that means, if we have to fix internal energy or enthalpy, we need two variables which automatically implies that both C_p and C_v are actually going to change, when two of these variables are changed either temperature pressure.

They may be weak functions of temperature and pressure in certain cases, but nevertheless thermodynamically they are going to be functions of two variables for a system, a single phase system containing one chemical species.

So, one of the challenges then, is to understand how the PVT behaviour of a substance plays a role in these calculations. So, to be able to do that, we start off with the simplest possible fluid an ideal gas, but before we go to the ideal gas one can look at another

simple application of the PVT behaviour and then we move on to the ideal gas type of behaviour.

So, then what I am interested in, is to try to obtain a relation for P V and T, in terms of variables that can be used in the calculations.

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Single phase region $V = V\{P, T\}$ $f\{P, V, T\} = 0$

$$dV = \left. \frac{\partial V}{\partial P} \right|_T dP + \left. \frac{\partial V}{\partial T} \right|_P dT$$

$$\frac{dV}{V} = \underbrace{\frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P}_{\beta} dT + \underbrace{\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T}_{-\kappa} dP$$

$$\frac{dV}{V} = \beta dT - \kappa dP$$

Volume expansivity β Isothermal Compressibility κ

$\beta = \kappa = 0$ for incompressible fluid

weak functions of T & P

So, for a single phase region, containing one chemical species, the volume is going to be a function of two variable, let us say temperature and pressure. Since, we are talking about PVT behaviour, let us express volume as a function of temperature and pressure.

So, these curly braces is something I am going to a use throughout this course. I am going to a use them to express the functionality, so volume depends on pressure and temperature or it is a function of pressure and temperature. So, I am going to a use this curly brace, braces to express that functionality or in other words I can also write this as function of PVT is going to be 0, mathematically they are equivalent statements, right. And if I take this and try to take the derivative, how much is the change in volume if both pressure and temperature change.

The way we express it mathematically is d V is going to be the partial derivative of V with respect to pressure right, the partial derivative of V with respect to pressure at constant temperature times d P plus, plus the partial derivative of the volume with respect to temperature at constant pressure this time. So, remember we said the vertical

bar is to denote the variables we are holding constant, we write those variables after the vertical bar in a subscript. And then we are taking the partial derivative of volume with respect to temperature at constant pressure times $d T$.

Since, V is a function of two variables P and T , I can express the total derivative in V as sum of these two partial derivatives $d \text{ou } V \text{ by } d \text{ou } P$ at constant temperature times $d P$ plus $d \text{ou } V \text{ by } d \text{ou } T$ at constant pressure times, times $d T$.

Now, if I take or if I divide this with volume $d V$ by V , there will be equal to 1 over V derivative of V , I am going to bring this term here with respect to $T d T$ plus the derivative of V with respect to P . This is this term brought here at constant temperature times $T P$.

So, all I have done is divided the above equation with V to get this expression, right. And what we are going to do is give a name to these two variables. This variable here, we will call this as β and this variable here we will call it as κ . So, then this will be β times $d T$. In fact, we will call this variable as negative κ , so that, this will be minus κ times $d P$.

So, then $d V \text{ by } V$ equals β times $d T$ minus κ times $d P$ minus κ times $d P$. So, these two variables here are called as volume expansivity. Say amount of volume expansion that takes due to change in temperature in those coordinates. It is actually the fractional volume change due to the change in temperature.

And then this κ here κ is called as the isothermal compressibility; isothermal compressibility. So, it is the change or the fractional change in volume due to the change in pressure $d \text{ou } V \text{ by } d \text{ou } P$ times 1 over V . So, if I increase the pressure the volume is going to decrease. So, that is the reason for having the negative sign therefore, κ , so it is the isothermal compressibility.

So, what we have done is we have expressed the fractional change in volume on the left hand side, as change in temperature plus a change in pressure multiplied with two coefficients which we are calling as volume expansivity and isothermal compressibility. Now, the reason we do this, is because for most for, for most liquids for small changes, we can actually consider them to be incompressible fluids. And if they are incompressible then this, both this coefficients right, both this coefficients β and

Kappa are going to be equal to 0 for incompressible fluids. Or even otherwise, if they are not completely equal to 0, these numbers are very small and they can be assumed to be weak functions of temperature and pressure.

So, they are going to be fairly constant for moderate changes in temperature and pressure and that affords us to calculate the change in volume fairly easily using the coefficients without resorting to elaborate integration schemes.

So, that is the reason, we like this expression, especially for liquids, if they are incompressible it is 0 anyway, otherwise I can take them to be weak functions of temperature and pressure and then I can easily integrate the expression and do some straight forward calculations.

So, we do not require any special PVT relationship or we are doing is expressing the change in volume, in terms of volume expansivity and isothermal compressibility.

And then I am going to use the fact that they are going to be weak functions of temperature and pressure and try to integrate these expressions for moderate changes in temperature and pressure and can make some quick calculations for liquids. So, let us see how we can do that through an example.

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Example

- At 353 K, and 1 bar the density, volume expansivity and isothermal compressibility for liquid water are $\rho = 972 \text{ kg m}^{-3}$, $\beta = 641 \times 10^{-6} \text{ K}^{-1}$ and $\kappa = 46.1 \times 10^{-6} \text{ bar}^{-1}$.

(a) To what pressure must the water be compressed to obtain a density of 973 kg m^{-3} at 353 K? Assume that κ is independent of P.

(b) To what temperature must the water be cooled to obtain a density of 973 kg m^{-3} at 1 bar? Assume that β is independent of T.

$$\frac{dV}{V} = \beta dT - \kappa dP \Rightarrow \frac{dV}{V} = -\kappa dP$$

$$V = V_e \Rightarrow \frac{dV}{V} = \frac{d(V_e)}{V_e} = \frac{-\frac{1}{\rho^2} d\rho}{\frac{1}{\rho}} = -\frac{d\rho}{\rho}$$

$$-\frac{d\rho}{\rho} = -\kappa dP \Rightarrow \frac{d\rho}{\rho} = \kappa dP \Rightarrow \ln \frac{\rho_2}{\rho_1} = \kappa (P_2 - P_1)$$

$$\int_{\rho_1}^{\rho_2} \frac{d\rho}{\rho} = \kappa \int_{P_1}^{P_2} dP$$

So, what I have is for a liquid water at 353 Kelvin in 1 bar the density isothermal compressibility. And volume expansivity are given to me, right the density is 972 the iso

volume expansivity is 641 and isothermal compressibility is $46.10 \times 10^{-6} \text{ bar}^{-1}$ inverse, right.

First question says to what pressure must water will be compressed to obtain a density of 973. So, this is water, it has a density of 972 kg per metre cube at 80 or 353 Kelvin. And we want to increase the pressure, so that the density increases slightly from 972 to began with 973 after the increase in pressure.

What we are interested in finding is how much should this change in pressure be or what should be the new pressure, so that the density will be 973, the temperature is still the same. And for this calculation we, we are told that we can assume that β is independent of β , β is independent of a pressure. So, to do this what we will do is, resort to the equation we had earlier, which says $\frac{dV}{V}$ is β times dT minus β times dP , right.

And then since the temperature is same 353 Kelvin, we are looking at case a here this 1. So, since the temperature is same I can drop the first term, there is no dT . So, it essentially means $\frac{dV}{V}$ for this scenario is simply minus βdP .

And since, we are talking about densities, I can either convert the density 973 to volume or other way of doing it is convert this β equation in terms of density itself. We know that the mole or volume V is 1 over the density, I am sorry this is the specific volume V is 1 over the specific density. So, $\frac{dV}{V}$ will be d of 1 over density by the density, so that will be 1 over ρ^2 $d\rho$ over sorry 1 over ρ here for volume.

So, this is 1 over ρ , so that will be minus $\frac{d\rho}{\rho}$. So, this is $\frac{dV}{V}$ which means, which means in terms of density negative of $\frac{d\rho}{\rho}$ is going to be negative of β times dP or $\frac{d\rho}{\rho}$ is going to be β times dP .

Now I can integrate this from the initial state through the final state which gives me logarithm of the final density over the initial density is going to be β times P_2 minus P_1 . I could do this, because I am assuming β , right, I am assuming this β to be independent of pressure, so when I integrate what I do is I go from ρ_1 to ρ_2 $\frac{d\rho}{\rho}$ equals β comes out of the integral P_1 to P_2 , initial pressure to the final pressure dP . So, this will give me this equation here, right.

So, I have the I have everything I need, I just need to calculate P 2. I just need to calculate P 2, the final pressure. So, the equation I had obtained so far is, logarithm of the ratio of the densities is K times, Kappa times P 2 minus P 1.

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$$\ln \frac{\rho_2}{\rho_1} = \kappa (P_2 - P_1) \Rightarrow P_2 = \frac{\ln(\rho_2/\rho_1)}{\kappa} + P_1 = \frac{\ln(973/972)}{46.1 \times 10^{-6}} + 1$$

$$= 23.3 \text{ bar}$$

(b) $\frac{dV}{V} = \beta dT - \kappa dT$ P is const. $\Rightarrow \frac{dV}{V} = \beta dT$

$$\frac{d(\rho/\rho_0)}{(\rho/\rho_0)} = \beta dT \Rightarrow \frac{-d\rho}{\rho^2} \times \rho_0 = \beta dT \Rightarrow \frac{d\rho}{\rho} = -\beta dT$$

$$\Rightarrow \ln\left(\frac{\rho_2}{\rho_1}\right) = -\beta(T_2 - T_1) \Rightarrow T_2 - T_1 = \frac{\ln\left(\frac{\rho_2}{\rho_1}\right)}{\beta}$$

$$\Rightarrow T_2 = T_1 - \frac{\ln\left(\frac{\rho_2}{\rho_1}\right)}{\beta} = 353 - \frac{\ln(973/972)}{641 \times 10^{-6}}$$

$$= \underline{351.4 \text{ K}}$$

So, what I am interested in is P 2. So, this is going to be logarithm of rho 2 over rho 1 divided by kappa, divided by Kappa plus plus P 1.

So, this is going to be logarithm of the final density is 973 kg per meter cube, the initial density is 972 kg per meter cube over the Kappa value given to us is 46.1 10 power minus 6 bar inverse. So, I am dividing with bar inverse. So, this whole term here will be in terms of bar. So, I just need to make sure that P 1 also is in terms of bar, the initial pressure was 1 bar.

So, if I simplify the numerical value what I get is 23.3 bar. So, I have to change the density from 1 bar to 23.3 bar, so that I am sorry, I have to change the pressure from 1 bar to 23.3 bar, so that the density changes from 972 to 973 are Kelvin that, sorry kg per meter cube.

So, that is a pretty straight forward calculation using, using the information given to us, right. Only thing to keep in mind is when we use these things, we are assuming of course, that Kappa is independent of pressure and then I could do the integration pretty easily. Sometimes we can also take a weak functionality in terms of pressure if there is

enough information and we can still do a similar type of integration if that information is available.

Now, let us look at the second part of this question, it says to what temperature must water be cooled to obtain the density of 973 kg per metre cube at 1 bar. So, in the second case; in the second case, in the second case I still need to get 973 Kelvin, but this time the pressure is held constant at 1 bar and we are changing the temperature.

The initial pressure is 1 bar, the final pressure is 1 bar, but I am changing the temperature now. So, we want to know what temperature should I cool this liquid to, so that the density will be 973 or density will change to 973 from 972. We still imply the same equation as earlier to begin with and then we will get rid of the terms we do not need in this particular case.

So, the equation we start with is $\frac{dV}{V} = \frac{dV}{V} = \beta \Delta T - \kappa \Delta P$. Now in this case, P is constant which implies $\frac{dV}{V}$ is simply going to be equal to $\beta \Delta T$, because dV is constant P is constant d term drops out. So, $\frac{dV}{V}$ is going to be $\beta \Delta T$.

Now, we can integrate this and then in this case we are told that β is independent of temperature, so we can integrate this, but before we do that let us change the volume into density, because that is the information we have. So, this will be equal to $\beta \Delta T$. Like earlier this will be derivative of $\ln(\rho)$ is going to be equal to $\beta \Delta T$ or $\frac{d\rho}{\rho} = \beta \Delta T$ or $\ln(\rho_2) - \ln(\rho_1) = \beta(T_2 - T_1)$ integrated from ρ_2 to ρ_1 and the second integral goes from T_1 to T_2 .

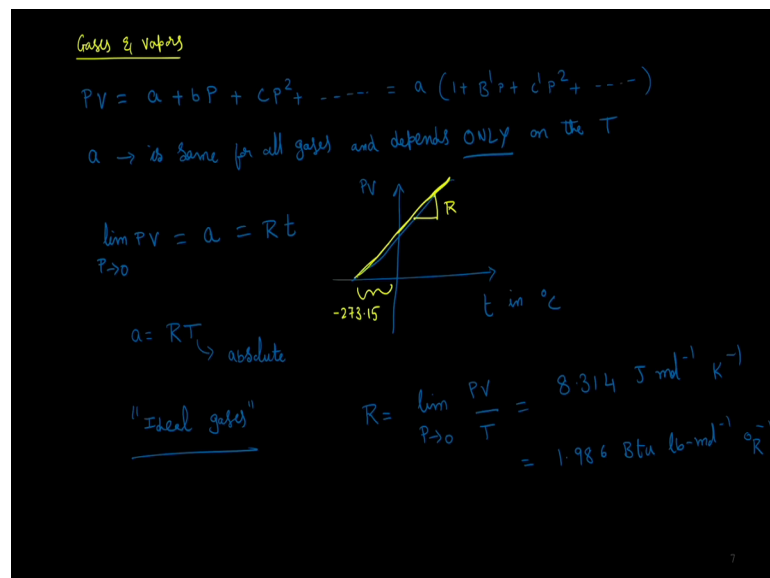
So, this will be $T_2 - T_1$, right or this means $T_2 - T_1$ is going to be $\ln(\rho_2) - \ln(\rho_1)$ divided by β . So, and then of course, I get a negative sign, I get a negative sign with the β . So, the negative sign appears there or T_2 is going to be $T_1 - \ln(\rho_2) - \ln(\rho_1)$ divided by β .

Now, I can plug in the numbers I already have, were starting at a temperature of 353 Kelvin minus \ln of 973 is the final density kg per meter cube 972 is initial density, also in kg per metre cube divided by β in Kelvin. So, $\frac{1}{\beta}$ is, sorry β in Kelvin inverse, so $\frac{1}{\beta}$ is going to be equal to, will be in terms of Kelvin and then I can add it to T_1 in Kelvin.

Let us see quickly get the value for beta, how much do we have? Beta is $641 \cdot 10^{-6}$ Kelvin inverse. So, that is $641 \cdot 10^{-6}$ Kelvin inverse. And if you simplify the numericals the final value we have is 351.4 Kelvin. So, all I need to do is, change the temperature from 353 to 351 Kelvin and will have the required change in density.

Now, compare this, for the same change in density which is going to obtain only if I change the pressure from 1 bar to 23.3 bar. So, I need to change the pressure a lot more than temperature to obtain the same change in density almost under identical, similar conditions. Having said this however, in most cases though, we do have a situation where this P V T relationship or such simple P V T relationships may not be applicable and what we are going to do is, try to see how we handle such scenarios.

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For most gases right, for most gases in the gas and vapour regions, the pressure volume product of pressure and volume can be expressed in terms of a power series in pressure a plus b p plus c p square plus an infinite series so on. And we can take this a out of the summation to get a 1 plus B prime P plus C prime P square plus so on in the infinite series.

This was observed to be true for most gases and vapours, right. For most gases and vapours such a infinite series relation seems to hold, right. And it was also observed that a is same for all gases and depends only on the temperature.

So, irrespective of the gas, this constant a seems to be same for all the gases and it depends only on temperature, right. And if I take the limit to get this value a all I need to do is take the limit as P goes to 0. If I take the limit for this product $P V$ as P goes to 0 or obtain this product at fairly low pressures as P goes to 0, then all the terms in the infinite series disappear except the first and this term is going to be equal to a , and for all the gases, this was observed to be R times, R times the temperature.

This temperature could be in any scale, there is no requirement for absolute temperature, but if we plotted in centigrade scale. We have discussed this earlier if we plot it in centigrade scale, a $P V$ relationship, right on y axis, we plot $P V$ on x axis we plot T integrate, centigrade then what I get is a straight line like that. Let us draw that in a different colour what I get is a straight line like that right.

The slope of this straight line is r and this intercept, if T is integrate centigrade it turns out to be negative 273.15, right. I can use different temperature units, I get different, different intercepts, right. And to get rid of the inconvenient number, what is often done is, express it the temperature in absolute units; such that you know a is going to be simply equal to R times T , T is an absolute units, absolute temperature either in Kelvin or raunchy, so that we do not have to worry about this intercept, that will make the intercept 0 for when we use the absolute scale.

And the such gases where at the limit of pressure going to 0 when $P V$ is going to be simply equal to $R T$, we call such gases as ideal gases. And if we want to get the value of R , then it would simply be the limit of P going to 0, the product $P V$ over T , this will be the value of R . And like we discussed earlier the value of R is 8.314 joules per mole per Kelvin, it is also equal to 1.986 B t u in English units per pound mole per degree Rankine.

So, what we are saying then is all the gases and vapours the product $P V$ can be expressed as an infinite series in P . And at the limit of 0 pressure all the terms disappear and $P V$ is going to be equal to $R T$ and we call such a behaviour as an ideal gas behaviour.

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The image shows handwritten notes on a blackboard. At the top, it defines the compressibility factor $Z = \frac{PV}{RT}$ and notes it is the "Compressibility factor". Below this, it states $Z = 1$ for ideal gases. Two virial equations of state are shown: one in terms of pressure, $Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + \dots$, and one in terms of volume, $Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$. A bracket on the right groups these two equations under the label "Virial EoS" with an arrow pointing to "Equation of State".

The other term we commonly encounter in thermodynamics is this ratio Z which is $P V$ over $R T$ and because of the definition of an ideal gas, if $P V$ equals $R T$ then this compressibility factor Z will be equal to 1. Will first write this name this is not to be confused with the isothermal compressibility this is Z and we call this as the compressibility factor.

And for ideal gases of course in $P V$ is $R T$ Z will always be equal to 1 for ideal gases. Otherwise, in terms of the power series, we have written earlier in terms of the power series, we have written earlier $P V$ over $R T$ will be equal to 1 plus the B prime coefficient times P plus C prime coefficient times P square and so on.

So, this compressibility factor is going to be this or we can also rewrite this in terms of volumes it will be Z equals 1 plus B by V , it still $P V$ over $R T$, we are simply changing the coefficients. So, that we can get this expression for the compressibility factor in terms of volume rather than pressure and in that case, it will be 1 plus P by V plus C by V squared plus so, on in the infinite series

These two infinite series expansions the coefficients B prime and B of course, are going to be related, we can derive a relation between them, but then for now it is sufficient to remember that these type of infinite series expansions are called as virial equation of state. Equation of state simply denotes, equation of state simply denotes that you are using it as a function to relate the PVT behaviour of a substance. And virial equation of

state is a type of equation of state where in we express the compressibility factor or $P V$ by $R T$ in terms of an infinite series of in P or 1 over V .

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$PV = RT \quad Z = 1 \quad (\text{ideal gas})$
 $\lim_{P \rightarrow 0} \quad V \rightarrow \infty$
 Simple $P \rightarrow 0$, $C = 1$, $F = 1 - 1 + 2 = 2 \quad U = U\{T, P\}$
 $U = U\{T\}$
 $C_V = \left. \frac{\partial U}{\partial T} \right|_V \equiv \frac{dU}{dT} \Rightarrow \begin{cases} C_V = C_V\{T\} \\ U = U\{T\} \\ \Delta U = \int_{T_1}^{T_2} C_V dT \end{cases}$

We will come back to the discussion on Virial equation of state and other types of equation of state later on, but for our discussion, now we will focus on the ideal gas behaviour and we said for an ideal gas $P V$ equals $R T$ and Z equals 1 for an ideal gas, right. And this occurs, because the infinite series, all the terms in the infinite series except the first one drop out and that happens at the limit of 0 pressure and at the at this limit all the gases are going to behave as ideal gases, right.

So, at this limit, since the pressure is 0 , right if you take this expression the volume is going to go to infinity which means the molecules are going to be very very far away. If the molecules are far away there is going to be almost negligible molecular interaction. The volume is so, large that the molecular interaction, interactions are negligible. There will not be a there will not be enough, there will not be large interactions between the molecules, because they are very far away, right.

The interactions decrease as the distance between the two molecules increases. Also compared to the volume, we are talking about the size of the molecules is going to be become negligible. There they will not occupy, almost they will occupy negligible volume as compared to the whole volume, we are talking about, we are talking about a very large volume. So, the size of the molecules is negligible compared to the total

volume. And also the molecular interactions are negligible and this characterizes the ideal gas behaviour.

Now, notice that using the phase rho for a single phase system. In general for a single phase system containing one chemical species, the degree of freedom is 1 minus the number of phases which is also 1 plus 2 or 2 for a single phase system containing one chemical species, the degrees of freedom is 2, right, but So, for example, if I have internal energy, then internal energy is fixed only if I fix 2 intensive variables, let us say temperature and pressure.

So, the internal energy of a gas, then if it is a single gas then is going to depend on two variables temperature and pressure, but for an ideal gas since, the intermolecular forces are negligible the change in pressure is not going to effect the internal energy, right.

Remember internal energy we said is due to vibration rotation of molecules translation of molecules which are all due to temperature that is where we get the translation rotation and vibration of molecules from. The bonding energy is which have nothing to do with the pressure the only thing that the pressure will effect is the potential energy or the intermolecular interactions, but because the intermolecular interactions in, in an ideal gas are so, small or negligible, pressure is not going to effect the internal energy. So, for an ideal gas U is going to be only a function of temperature, it will not depend on pressure, because inter molecular interactions are negligible, right in fact 0.

So, for an ideal gas, let us use a super script $i g$ for the ideal gas. Then it will depend only, only on temperature. Now see what happens, if the functionality is only in terms of temperature is the derivative C_v . Remember, we defined it as the partial derivative of the molar internal energy with respect to temperature at constant volume; at constant volume.

We need a partial derivative, if there is, if, if U depends on more than one variable, but now U depends only one variable that is temperature. So, we do not need partial derivative any more. For an ideal gas than it will simply be dU over dT , dU over dT , right. So, C_v for an ideal gas than is going to be a function only of temperature, U for an ideal gas is going to be only a function of temperature and ΔU is going to be simply $C_{v i g} dT$.

Irrespective of whether the volume is constant or not it does not matter, because U depends only on temperature, ΔU is going to be $\int C_v dT$ always, this is true for an ideal gas.

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The image shows a handwritten derivation on a blackboard. At the top left, the word "Enthalpy" is underlined in yellow. The first line shows $U^{ig} = U^{ig}\{T\}$ and $C_v^{ig} = \frac{dU^{ig}}{dT}$. The second line shows $H^{ig} = U^{ig} + PV^{ig} = U^{ig} + RT \Rightarrow H^{ig} = H^{ig}\{T\}$, with a yellow arrow pointing from the U^{ig} term in the first line to the U^{ig} term in the second line. The third line shows $C_p^{ig} = \left. \frac{\partial H^{ig}}{\partial T} \right|_P = \frac{dH^{ig}}{dT}$. The fourth line shows $C_p^{ig} = \frac{dH^{ig}}{dT} = \frac{d(U^{ig} + RT)}{dT} = \frac{dU^{ig}}{dT} + R = C_v^{ig} + R$. At the bottom, the equation $C_p^{ig} - C_v^{ig} = R$ is boxed in blue. A small number "19" is visible in the bottom right corner of the blackboard image.

Now, let us look at what happens, what happens to enthalpy. We had U for an ideal gas to be a function only of Temperature we also have C_v for an ideal gas defined as dU for an ideal gas over dT .

Now, let us look at enthalpy by definition enthalpy is u plus PV . And for an ideal gas, I can just use a subscript ig for the 3 variables H , U and V right. And since, this term for an ideal gas is RT PV is RT so, this term is RT . So, then this will be U_{ig} plus RT . Now u is a function only of temperature as we have seen here right. And RT only has temperature which then implies H also will be a function of temperature alone for the ideal gas.

And by definition the specific heat capacity C_p is the partial derivative of H with respect to temperature at constant pressure than for an ideal gas, because it depends only on one variable the partial derivative reduces to the total derivative, it will be dH_{ig} over dT , that will be the value of $C_{p,ig}$, right.

So, these are the two relations, we get for an ideal gas that both internal energy and enthalpy then are going to be only the functions of temperature, we can also derive a

relationship between these two C_p and C_v between these two specific heat $C_{p,i,g}$ and $C_{v,i,g}$, right, for example, $C_{p,i,g}$ is $dH_{i,g} / dT$ so, this is $dU_{i,g} / dT$ plus R .

So, this will be $dU_{i,g} / dT$ plus the derivative of RT with respect to dT will be R . And the first term is $C_{v,i,g}$ if you recall so, $C_{p,i,g}$ will then be equal to $C_{v,i,g}$ plus R or usually the way we write it is the difference between the two specific heats. In case of an ideal gas is going to be equal to the gas constant R .

So, then we looked at small manipulations involving the internal energy and enthalpy for an ideal gas type of a behaviour. The most important thing to remember here is that both these quantities enthalpy and internal energy. And hence, their derivatives with respect to temperature $C_{p,i,g}$ and $C_{v,i,g}$ are going to depend only on temperature, if the behaviour is like an ideal gas.

Now, what we will do is we will try to do some calculations involving heat work and the internal energy as well as the enthalpy changes for some of the processes that we commonly encounter in an industry. So, the first type of process, we will look at today is, what we call as an isothermal process.

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Isothermal Process involving an ideal gas.
 T is const. $\Delta U = \Delta H = 0$
 $dU = dQ + dW \Rightarrow dQ = -dW = PdV$
 $dQ = PdV = \frac{RT}{V} dV \Rightarrow Q = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln \frac{V_2}{V_1}$
 $dW = -RT \ln \frac{V_2}{V_1}$

We are going to stick our discussion to ideal gases for different types of processes. And isothermal process involving an ideal gas right, if it is an isothermal process temperature is constant, right that is a characteristic of an isothermal process. And if temperature is

constant then both ΔU as well as ΔH for an ideal gas is going to be 0, because the temperature is not changing and both these quantities depend only on temperature. If temperature does not change Δ in these quantities is going to be 0.

Also, since the first law applies, we are talking about a closed system. Since the first law applies and since dQ is a sorry, dU is dQ plus dW this implies dQ is negative of dW and this will be equal to $P dV$ for a reversible, for a reversible process, right. And this is an ideal gas, right. So, dQ is $P dV$ for an ideal gas P is $R T$ by V . So, $R T$ by $V dV$ and if I integrate, this is an isothermal process. So, Q is going to be integral of $R T$ over $V dV$ going from volume 1 to volume 2.

Since, temperature is constant, it can come out of the integral and what I will have inside the integral is simply dV over V going from V_1 to V_2 , going from V_1 to V_2 and. And, if I finish this integral, it will be $R T \ln V_2$ over V_1 . Now let us look at another process involving an ideal gas, this time an isobaric process, isobaric process involving an ideal gas.

The process is isobaric which means temperature will change what will be constant is the pressure, the pressure is constant what happens to the process?

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Isobaric process involving an ideal gas.

$$\Delta U^{ig} = \int_{T_1}^{T_2} C_V^{ig} dT \quad \Delta H^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT$$

$$dW = -PdV = -P d(RT/P) = -RdT$$

$$\Rightarrow W = -\int_{T_1}^{T_2} R dT = -R(T_2 - T_1)$$

$$\Delta U = Q + W \Rightarrow Q = \Delta U - W = \Delta U - R\Delta T = \Delta H$$

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Delta U is simply going to be integral of C_V dT going from T₁ to T₂ for the ideal gas. And delta H is going to be integral going from T₁ to T₂ C_P dT. Depending on the values of C_P and C_V, we can integrate this and get delta H or delta U, right.

What happens to dU, dQ, dW what happens to the work done W if the process is reversible then dW is going to be negative, negative of P dV, right.

And since, the pressure is constant, right, it will be negative of P, we will write dV as R T over P, because this is an ideal gas P V is R T or V is R T over P, now P and R are constants so, it will be minus R dT.

This is dW or if we integrate this going from T₁ to T₂, we will get W as integral going from T₁ to T₂ negative R dT or this is R negative R T₂ minus T₁, this is W. And dU we already have so, Q since delta U is Q plus W, we can get Q. Once we get the integral for C_V dT, we can then calculate Q as delta U minus, minus W, it also turns out that since this is an ideal gas P V is RT.

So, once we put this delta U minus R R delta T, this will be actually equal to delta H. So, for an ideal gas than if the process is isobaric Q is going to be equal to delta H, W is going to be negative R delta T and we can calculate delta H and delta U from the integrals.

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Handwritten equations on a blackboard:

Isochoric process involving an ideal gas

$$\Delta U^{ig} = \int_{T_1}^{T_2} C_V^{ig} dT \quad \Delta H^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT$$

$$dW = -P dV = 0$$

$$\Delta U = Q + W \Rightarrow Q = \Delta U^{ig}$$

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The third type of process, we want to look at is what we call as an isochoric process involving an ideal gas again. In case of an isochoric process, we go back to our earlier expressions. Since, temperature is changing ΔU is going to be integral $C_V dT$ and ΔH is going to be integral $C_P dT$. If the process is also reversible then dW is going to be $-P dV$ and because it is an isochoric process, this will be 0. Since for a closed system the first law applies $\Delta U = Q + W$. And since W is 0, it implies the heat exchange will be equal to the internal energy change which is ΔU all through of course, we mean an ideal gas.

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Adiabatic Process involving ideal gases

$$dQ = 0 \quad dU = dW \Rightarrow C_V dT = -P dV$$

$$\Rightarrow C_V dT = -\left(\frac{RT}{V}\right) dV \Rightarrow \frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V} \Rightarrow \ln \frac{T_2}{T_1} = -\frac{R}{C_V} \ln \frac{V_2}{V_1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P}$$

$$dT = d\left(\frac{PV}{R}\right)$$

$$\frac{P_2}{P_1} = \left(\frac{V_2}{V_1}\right)^{C_P/C_V}$$

The last type of process, we want to look at is what we call as an adiabatic process. And again these equations are applicable only for adiabatic processes involving ideal gases. And all the equations earlier as well we always said that work done is calculated only for a reversible process so, that statement also holds.

We are talking about a reversible adiabatic process involving ideal gas, because the process is adiabatic, no heat is exchanged with the surroundings. So, dQ is always 0 and applying the first law it means that dU is going to be equal to dW , dU is going to be equal to dW . And this implies $C_V dT$, because this is an ideal gas dU is always going to be $C_V dT$. And on the other side dW is always going to be equal to minus, minus $P dV$, because it is a reversible process, because it is also a process that involves ideal gas, I can write this as minus $R T \ln \frac{V_2}{V_1}$.

So, we will rearrange the terms a little bit dT/T will be negative $R/C_v dV/V$ which implies $\ln(T_2/T_1)$ is negative $R/C_v \ln(V_2/V_1)$. If I complete that integration going from T_1 to T_2 to V_1 to V_2 .

Or in other words if I get rid of the logarithms it turns out T_2/T_1 is going to be V_1/V_2 to the power R/C_v . This of course, is still for an ideal gas so, we will retain those superscripts C_v i g, I can rearrange the terms instead of volumes, I could have worked with pressures, and I could have obtained a similar equation involving pressure. So, what I mean by that is instead of writing, instead of writing this P for the ideal gas as $R T/V$, I could have changed the volume term here and written it as $R T/P$. And then rearrange the terms proceeded with the integration all the way through the end as we have done in case of volume. And what we would have obtained is a relation between the temperatures and pressures in an adiabatic process.

And that would look something like this I would leave it for you to work on, but it is pretty straight forward, all we will do is we will retain the P as it is and change V inside the derivative dV to $d(R T/P)$ and then start working with the manipulations so, that we can get the relation between temperatures and pressures.

In case of a reversible adiabatic process involving an ideal gas, we can also do another manipulation see, we have 3 variables for an ideal gas, we just need two intensive properties to fix the state of the system and to begin with we had C_v i g dT is a negative of $P dV$, right here right.

So, one way to rework these equations is substitute volume as $R T/P$, another ways to substitute P as $R T/V$, the third way would be to replace dT term on the left hand side. And write it as in terms of P and V , right in terms of P and V . So, $P V$ is $R T$ so, it will be $P V$ over $R dT$ will be $d(P V)$ over R .

So, I can use this substitution then what I end up finally, is a relation between P and V that involves an adiabatic process P and V . In case of an adiabatic process and it will look something like this P_2/P_1 is V_1/V_2 C_p/C_v . So, now, then let us change this colour just to make sure that we are relating one to another. So, this would be in yellow, right.

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Adiabatic process involving ideal gases

$$dQ = 0 \quad dU = dW \Rightarrow C_V^{ig} dT = -P dV \quad \frac{RT}{P}$$

$$\Rightarrow C_V^{ig} dT = -\left(\frac{RT}{V}\right) dV \Rightarrow \frac{dT}{T} = -\frac{R}{C_V^{ig}} \frac{dV}{V} \Rightarrow \ln \frac{T_2}{T_1} = -\frac{R}{C_V^{ig}} \ln \frac{V_2}{V_1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V^{ig}}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P^{ig}}$$

$$dT = d\left(\frac{PV}{R}\right)$$

$$\frac{P_2}{P_1} = \left(\frac{V_2}{V_1}\right)^{C_P/C_V}$$

ONLY for const. C_P^{ig} C_V^{ig}

So, this was T_2 over T_1 was P_2 over P_1 to the power R by C_p^{ig} . So, we get three equivalent relations, one involving temperature and volume the other one involving temperature and pressure, the third one involving pressure and volume. All equations are identical depending on the availability of data, we can use one of these equations to get the other unknowns.

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$$dU = dW + dQ \Rightarrow dU = dW \text{ (adiabatic)}$$

$$\Delta U^{ig} = W = \int_{T_1}^{T_2} C_V^{ig} dT$$

Polytropic process

$$\delta = 0 \text{ isobaric}$$

$$\delta = 1 \text{ isothermal}$$

$$\delta = \infty \text{ isochoric}$$

$$\delta = \frac{C_P}{C_V} \text{ adiabatic}$$

$PV = RT$

Now, what happens these are interrelationships between pressure volume and temperature in an adiabatic process. What happens to dW and dU , let us take a look at

them for an adiabatic process. dU is going to be equal to dW , because dQ is 0, dU for an adiabatic process is going to be equal to dW always. Now, this also involves a reversible process is also involves an ideal gas. So, dU is going to be or ΔU is going to be equal to W and this will be equal to integral of $C_{v,i} dT$ going from T_1 to T_2 .

I can write this in a variety of forms depending on the relationships, we have obtained earlier and then use whatever information is available to get the work done. So, essentially that is the summary of using an ideal gas for a variety of processes, there is also something called as a polytropic process that is mentioned in the box.

It essentially is one of these earlier processes, we have discussed and it is expressed using a parameter γ and depending on the value of γ the polytropic process reduces, reduces to one of the processes we discussed for example, γ is 0, it will be an isobaric process, if γ is 1 it will be an isothermal process, right.

And then if γ equals infinity it will be an isochoric process and if γ equals C_p over C_v , it will be an adiabatic process, this ratio C_p over C_v is often called as γ the ratio of the specific heats for an ideal gas.

While we write it, I should also mention that the relations, we derived earlier that involve temperature and volume relation or temperature. And pressure relation these are applicable only for constant specific heat capacity $C_{p,i}$ and $C_{v,i}$ have to be constant, they cannot change with temperature that is when we can write these expressions, right.

There are some books which involve a relation between $P V T$ involving a polytropic process and depending on the value of γ , we get the correct relationships, but then the basic idea of using an ideal gas is that we express the $P V T$ relationship as $P V^\gamma = R T$. And depending on the nature of the process I can work with the first law and obtain the work done heat exchanged as well as ΔU and ΔH for any of the processes.

Once I know that this relationship is applicable and we have demonstrated few of those processes. In this discussion today, what we will do when we come back in the next lecture is try to use these ideas and do some numerical calculations on various processes involving an ideal gas as well as also try to look at how we handle irreversibility or one of the ways to handle irreversibility because for the discussion so far we have always talked about a reversible process. What happens if there is an irreversibility, how would I

handle irreversibility in a process that involves an ideal gas? So much for today and thank you for listening to the lecture so far, I will see you in the next one.