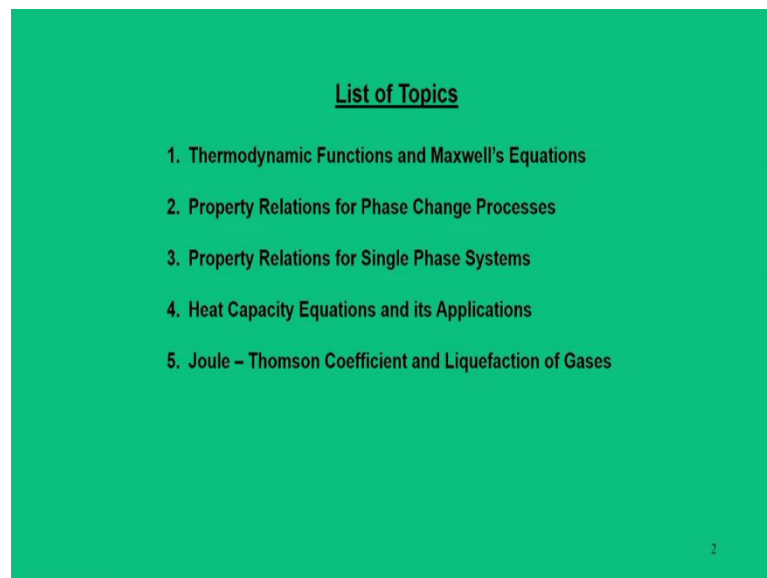


Advanced Thermodynamics and Combustion
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Module - 03
Thermodynamic Property Relations
Lecture - 13
Heat Capacity Equations and its Applications

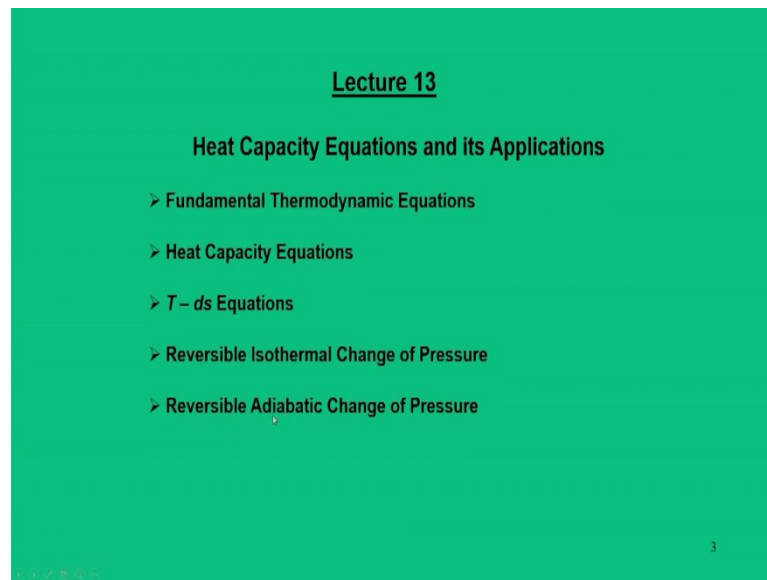
Dear learners, greetings from IIT Guwahati we are in the course Advanced Thermodynamics and Combustions module 3 Thermodynamic Property Relations.

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Till this point of time, we have completed three lectures thermodynamic functions and Maxwell equations. Lecture number 2, property relations for phase change processes, lecture number 3 is for property relations for single phase systems. We are now in the lecture number 4, which we are going to discuss today that is heat capacity equations and its applications.

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Lecture 13

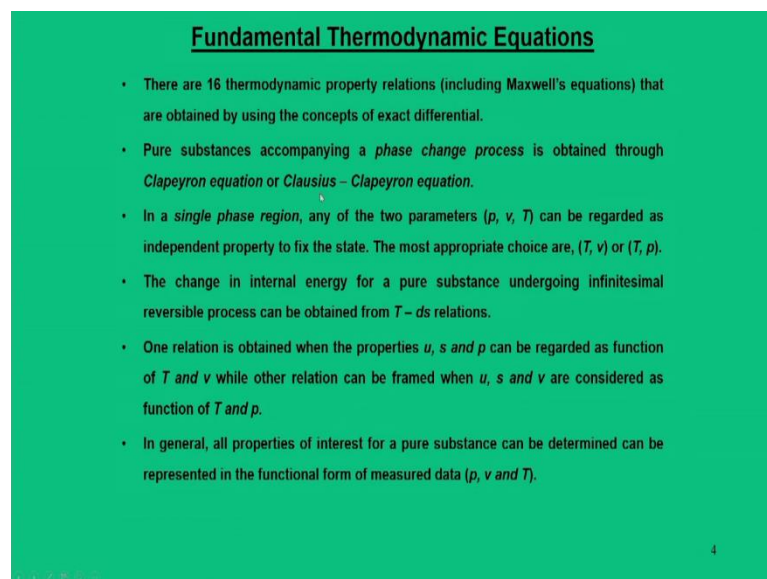
Heat Capacity Equations and its Applications

- Fundamental Thermodynamic Equations
- Heat Capacity Equations
- $T - ds$ Equations
- Reversible Isothermal Change of Pressure
- Reversible Adiabatic Change of Pressure

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So, in this lecture we will touch upon the following components, first is the fundamental thermodynamic equations what we have studied so far, we are going to summarize them. Then we will move on to another important equations or relations, which is known as $T ds$ equations as well as heat capacity equations. Then we are trying to use this heat capacity equations for certain situations and two situations we are going to discuss; one is for reversible isothermal change of pressure, second one is the reversible adiabatic change of pressures.

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Fundamental Thermodynamic Equations

- There are 16 thermodynamic property relations (including Maxwell's equations) that are obtained by using the concepts of exact differential.
- Pure substances accompanying a *phase change process* is obtained through *Clapeyron equation* or *Clausius - Clapeyron equation*.
- In a *single phase region*, any of the two parameters (p, v, T) can be regarded as independent property to fix the state. The most appropriate choice are, (T, v) or (T, p).
- The change in internal energy for a pure substance undergoing infinitesimal reversible process can be obtained from $T - ds$ relations.
- One relation is obtained when the properties u, s and p can be regarded as function of T and v while other relation can be framed when u, s and v are considered as function of T and p .
- In general, all properties of interest for a pure substance can be determined can be represented in the functional form of measured data (p, v and T).

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Now, let us move to the topic of our discussions that is the first segment the fundamental thermodynamic equations. So, till this point of time we know that the classical mathematical concepts has been used to obtain 16 thermodynamic property relations that includes Maxwell equations and all these equations use the concept of exact differentials.

Then we try to apply these equations for pure substances that accompany phase change process; so, there we derived Clapeyron equations and Clausius-Clapeyron equations. Now, when we apply these relations for a single-phase regions in which we require at least two state coordinates out of pressure, volume and temperatures. And the most appropriate choice among these three are either temperature volume or temperature pressure.

Then based on this we obtain one relations in which the properties u, s, and p are regarded as a function of temperature and volume, other relations we framed for temperature and pressures. And ultimately we told that all properties of interest for a pure substance can be determined as a functional form from the measured data which are pressure specific volume and temperatures. And we can find the other derived properties using this relations.

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Fundamental Thermodynamic Equations

- Basic Relations: $T \left(\frac{\partial u}{\partial s} \right)_v$ & $-p \left(\frac{\partial u}{\partial v} \right)_s$; $T \left(\frac{\partial h}{\partial s} \right)_p$ & $v \left(\frac{\partial h}{\partial p} \right)_s$;
- $-p \left(\frac{\partial \psi}{\partial v} \right)_T$ & $-s \left(\frac{\partial \psi}{\partial T} \right)_v$; $v \left(\frac{\partial g}{\partial p} \right)_T$ & $-s \left(\frac{\partial g}{\partial T} \right)_p$
- Maxwell Relations: $\left(\frac{\partial T}{\partial v} \right)_s = \left(\frac{\partial p}{\partial s} \right)_v$; $\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p$; $\left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T$; $\left(\frac{\partial v}{\partial T} \right)_p = \left(\frac{\partial s}{\partial p} \right)_T$
- Additional Relations: $\left(\frac{\partial u}{\partial s} \right)_v = \left(\frac{\partial h}{\partial s} \right)_p$; $\left(\frac{\partial u}{\partial v} \right)_s = \left(\frac{\partial \psi}{\partial v} \right)_T$; $\left(\frac{\partial h}{\partial p} \right)_s = \left(\frac{\partial g}{\partial p} \right)_T$; $\left(\frac{\partial \psi}{\partial T} \right)_v = \left(\frac{\partial g}{\partial T} \right)_p$

16 Relations among properties, Exact differentials

- Phase change process (Clapeyron Equation): $\left(\frac{dp}{dT} \right)_{sat} = \frac{h_g - h_f}{T(v_g - v_f)}$
- Clausius-Clapeyron Equation: $\left(\frac{dp}{dT} \right)_{sat} = \frac{h_g - h_f}{(RT^2/p)} \left[\frac{d(\ln p)}{dT} \right]_{sat} = \frac{h_g - h_f}{RT^2}$ ($\psi = RT$)
- Single phase systems: $\left(\frac{\partial u}{\partial T} \right)_v = c_v$; $\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p$; $\left(\frac{\partial h}{\partial T} \right)_p = c_p$; $\left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p$
- $s_2 - s_1 = \int_1^2 \frac{c_p}{T} dT + \int_1^2 \left(\frac{\partial p}{\partial T} \right)_v dv$; $u_2 - u_1 = \int_1^2 c_v dT + \int_1^2 \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv$
- $s_2 - s_1 = \int_1^2 \frac{c_p}{T} dT - \int_1^2 \left(\frac{\partial v}{\partial T} \right)_p dp$; $h_2 - h_1 = \int_1^2 c_p dT + \int_1^2 \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$
- Internal Energy Equations: $\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p$; $\left(\frac{\partial u}{\partial p} \right)_T = T \left(\frac{\partial v}{\partial T} \right)_p - v$

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Now, let us understands what are those relations, first 16 relations that comes as a basic-relations, Maxwell's equations, and some additional relations. So, these three category called as 16 thermodynamic relations among the properties. Now, these are derived through our concept of exact differential equation. Now, when these relations are applied for phase change process, we get Clapeyron equations and Clausius Clapeyron equations.

And this Clausius Clapeyron equations when you deal with the change of situations or state in a gaseous medium, we can assume this situation to be to be constant what is called as equation of state $pv = RT$. Then this two relations are for phase change process. Now, for a single phase system we derived the relations mainly the specific heat at constant volume and specific heat at constant pressure as a function of the entropy and internal energy. And also we found the internal energy equations from this relations.

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Heat Capacity Equations

- The presentation till this point is mainly concentrated towards developing thermodynamic relations that allow changes in u , h and s to be evaluated from measured data.
- Several other thermodynamic relations can be introduced which are defined in terms of some other property. Each of these properties has a common attribute. Specific heats for pure substances (c_p and c_v) are examples of these categories.
- Laboratory measurements of heat capacity of solids/liquids takes place normally at constant pressure and they are reported per unit mass. Because of thermal expansion, the specific heat at constant volume is normally ignored due to experimental measurement difficulties.
- Under such circumstances, mathematical expressions of c_p and c_v in terms of measurable quantities, play vital role. Some of the significant parameters are volume expansivity/coefficient of volume expansion and isothermal compressibility.

Isothermal compressibility: $\kappa = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_T$

Volume expansivity / Coefficient of volume expansion: $\beta = \left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial T}\right)_p$

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Now, let us understand the next important segment what we call as heat capacity equations. Many a times we all aware that the specific heat is one of the fundamental concept, and we see that specific heat means amount of energy required to change the temperature by unit degree kelvin or centigrade.

Now, we found that for substances like solid and liquid we have one specific heat, but specific heat for gases can have two, one is specific heat at constant pressure and specific heat at constant volume because, they follow the ideal gas equation of states where the change of state can happen through either at constant pressure or at constant volume.

But what happens is that most of the laboratory experiments when you define the specific heat capacity normally it is done at constant pressure. So, in fact, when you tell that specific heat of water by default it is assumed that we get the data when by keeping the pressure constant. And these laboratory datas are reported, but what happens that when you go to find out the specific heat at constant volume we normally ignore it. Because, it is very

difficult to maintain constant volume while changing the temperatures; so, there are experimental difficulties are involved.

Now because of this reasons; so, it is required that we should also formulate the expressions in which we can find out the specific heat at constant volume mathematically for pure substances; so, this is the importance of this relations. Now, apart from that we will be also using some other important properties which what we call as isothermal compressibility.

In fact, we have already discussed about this in our previous lectures. And this isothermal compressibility is defined by the term $\kappa = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_T$. Other parameter is volume expansivity or coefficient of volume expansion, $\beta = \left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial T}\right)_p$.

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Heat Capacity Equations

- Both temperature and pressure can be varied independently so that one can be varied keeping other constant.

Recall Equations: $ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv$ & $ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$

After subtraction: $(c_p - c_v) dT = T \left(\frac{\partial p}{\partial T}\right)_v dv + T \left(\frac{\partial v}{\partial T}\right)_p dp$

Take $p = p(T, v) \Rightarrow dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT$

Substitute dp , $\Rightarrow (c_p - c_v) dT = T \left(\frac{\partial p}{\partial T}\right)_v dv + T \left(\frac{\partial v}{\partial T}\right)_p \left[\left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT\right]$

$\Rightarrow \left[(c_p - c_v) - T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v\right] dT = T \left[\left(\frac{\partial p}{\partial T}\right)_v + \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T\right] dv$

If $dv = 0$ & $dT \neq 0 \Rightarrow (c_p - c_v) = T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v$ ✓

If $dv \neq 0$ & $dT = 0 \Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T \Rightarrow c_p - c_v = -T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T$

Recall, $\kappa = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_T$ & $\beta = \left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial T}\right)_p \Rightarrow c_p - c_v = v \left(\frac{T\beta^2}{\kappa}\right)$

Now, having said all these things let us try to see that how we can get the heat capacity equations, by heat capacity equations we assume that we are looking at specific heats at constant volume and constant pressures. Now, from our previous relations we can recall

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv \quad \& \quad ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$$

Now, what we do is from these two expressions if you subtract

$$(c_p - c_v)dT = T \left(\frac{\partial p}{\partial T} \right)_v dv + T \left(\frac{\partial v}{\partial T} \right)_p dp$$

Now, at this stage we have seen that left hand side is the temperature; right hand side is the specific volume and pressure. So, we can get all these relations or we can say that if you say pressure is a function of temperature and specific volume then we can find the expression of dp. Now, why do we require? Because, so, we want to get rid of this dp.

So, if you calculate exact differential of pressure

$$p = p(T, v) \Rightarrow dp = \left(\frac{\partial p}{\partial v} \right)_T dv + \left(\frac{\partial p}{\partial T} \right)_v dT$$

Now, when I substitute

$$(c_p - c_v)dT = T \left(\frac{\partial p}{\partial T} \right)_v dv + T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial v} \right)_T dv + T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v dT$$

Then what you do you simplify this equations; so, after simplifications we find this relation.

$$\left[(c_p - c_v) - T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v \right] dT = T \left[\left(\frac{\partial p}{\partial T} \right)_v + \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial v} \right)_T \right] dv$$

So, right hand side of this equations contains only specific volume and left-hand side of the equations contains the change in the temperature. So, we have already mentioned that temperature and volume can be varied independently by keeping other as constant.

$$\text{If } dv = 0 \& dT \neq 0 \Rightarrow (c_p - c_v) = T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v$$

$$\text{If } dv \neq 0 \& dT = 0 \Rightarrow \left(\frac{\partial p}{\partial T} \right)_v = - \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial v} \right)_T$$

Then we get the expressions $c_p - c_v = -T \left(\frac{\partial v}{\partial T} \right)_p^2 \left(\frac{\partial p}{\partial v} \right)_T$.

Now, here if I recall the $\kappa = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_T$ & $\beta = \left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial T}\right)_p$. So, we can find that $c_p - c_v = v\left(\frac{T\beta^2}{\kappa}\right)$. So, basically change in the specific heat is expressed in terms of isothermal compressibility.

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Heat Capacity Equations

- The general relation between c_p and c_v is often referred as Mayer equation.
- Several important consequences can be drawn from specific heat relations.

Recall Equations: $c_p - c_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial v}\right)_T = v\left(\frac{T\beta^2}{\kappa}\right)$

Case I: Ideal gas, $p = \frac{RT}{v} \Rightarrow \left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{v^2}$ & $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$

$$\Rightarrow c_p - c_v = (-T)\left(\frac{R}{p}\right)\left(\frac{R}{p}\right)\left(\frac{-RT}{v^2}\right) = v\left(\frac{v}{T}\right)\left(\frac{RT}{v^2}\right) = R$$

$\Rightarrow c_p - c_v = R$

Case II: κ is positive for all substances in all phases & β^2 is always positive $\Rightarrow c_p - c_v > 0$ or $c_p > c_v$

Case III: $T \rightarrow 0 \Rightarrow c_p = c_v$ at absolute zero

Case IV: $\left(\frac{\partial v}{\partial T}\right)_p \rightarrow 0 \Rightarrow c_p = c_v$ (Only one specific heat for solids/liquids)
(e.g. state of water at 4°C where density of water is maximum)

Now, let us find out some important consequences, but before I said this equation $c_p - c_v = v\left(\frac{T\beta^2}{\kappa}\right)$ is often referred as Mayer equation. Now, what is the significance of Mayer equations, let us find out the important consequence. Now, this relation is true for all the states of the substance say solid, liquid and gas phase.

Now, if I say in a situation that if your substance is an ideal gas where $pv = RT$. Then we can find out $\left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{v^2}$ & $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$. Now, when I put this expressions in the above relations; $c_p - c_v = (-T)\left(\frac{R}{p}\right)\left(\frac{R}{p}\right)\left(\frac{-RT}{v^2}\right) = v\left(\frac{v}{T}\right)\left(\frac{RT}{v^2}\right) = R$; R is nothing but the characteristics gas constant. So, here I need to emphasize that we all aware of this expressions $c_p - c_v = R$ for an ideal gas, but this is the mathematical proof that how we get the $c_p - c_v = R$ for an ideal gas.

Now, in the second case that is case 2, we are trying to prove that $c_p > c_v$, why? Because the term β^2 is always positive because it is square quantity, absolute temperature is positive and specific volume is also a positive number.

So, in fact, more importantly that kappa is positive for all substances in all phases this is an experimental evidence and because of this reason we say that $c_p - c_v > 0$ or $c_p > c_v$; which means, specific heat at constant pressure is always higher than the specific heat at constant volume. And third important consequence we can derive that when the temperature T goes to 0, then equation says that $c_p = c_v$ what it means that at absolute zero temperatures we do not have separate specific heat we have unique specific heats and because both c_p and c_v merge. And last important inference we can say that when $\left(\frac{\partial v}{\partial T}\right)_p \rightarrow 0$ then only $c_p = c_v$.

And this relation is true $\left(\frac{\partial v}{\partial T}\right)_p \rightarrow 0$ for solids and liquids. And because of this region we say $c_p = c_v$, one simple example says that when you say water at 4 C, the density of water is maximum and at that situation this tends to 0; so, this is all about the difference between c_p and c_v .

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Heat Capacity Equations

- Alternatively, the "specific heat ratio" is expressed as ratio of isothermal compressibility to isentropic compressibility of the substance.
- Speed of sound is another property that can be found from specific heat ratio for an ideal gas.

Recall T - ds Equations: $ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv$ & $ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$

At constant entropy, $c_p dT = T \left(\frac{\partial p}{\partial T}\right)_v dp$ & $c_v dT = T \left(\frac{\partial p}{\partial T}\right)_v dv$

Taking the ratio, $\frac{c_p}{c_v} = \frac{\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p} = \frac{\left(\frac{\partial p}{\partial v}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_p} = \frac{\left(\frac{\partial p}{\partial v}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_v} \left(\frac{c_p}{c_v}\right)$

Recall equations: $\kappa = \left(\frac{1}{v}\right) \left(\frac{\partial v}{\partial p}\right)_T$ & $\alpha = \left(\frac{1}{v}\right) \left(\frac{\partial v}{\partial T}\right)_p$; $\frac{c_p}{c_v} = \left(\frac{1}{\alpha v}\right) \left(\frac{\partial p}{\partial v}\right)_v = \frac{\kappa}{\alpha}$

κ : Isothermal compressibility; α : Isentropic compressibility; Ideal gas: $p = \frac{RT}{v} \Rightarrow \left(\frac{\partial p}{\partial v}\right)_v = \frac{-RT}{v^2}$

Speed of sound: $c = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s} = \sqrt{v^2 \left(\frac{\partial p}{\partial v}\right)_s} = \sqrt{v^2 \left(\frac{1}{\alpha v}\right)} = \sqrt{\frac{v}{\alpha}} = \sqrt{\frac{c_p}{c_v} \left(\frac{v}{\kappa}\right)}$

Ideal gas medium: $c = \sqrt{v^2 \left(\frac{\partial p}{\partial v}\right)_s} = \sqrt{v^2 \left(\frac{c_p}{c_v}\right) \left(\frac{\partial p}{\partial v}\right)_v} = \sqrt{\frac{c_p}{c_v}} RT$

$\frac{c_p}{c_v} \rightarrow \gamma$

$p, v, T \rightarrow$
cyclic relation

$\rho = \frac{1}{v}$

Now, another important term we all aware that we call this as a specific heat ratio $\frac{c_p}{c_v} = \gamma$. This ratio we are trying to express in the form of isothermal compressibility to isentropic compressibility for the pure substance; let us see how we are going to do that that is first thing.

Second important relations about this specific heat ratio is that, this has a definite bearing with a property parameter, which is known as speed of sound. In fact, speed of sound is a function of specific heat ratio for an ideal gas we all know it.

Now, let us see how we are going to get all these expressions; so, again here the first fundamental two equations we need to recall $ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv$ & $ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$. So, at constant entropy; that means, $ds = 0$; so, we get $c_p dT = T \left(\frac{\partial v}{\partial T}\right)_p dp$ & $c_v dT = -T \left(\frac{\partial p}{\partial T}\right)_v dv$.

Then; obviously, you need to find out the specific heat ratio then you take this ratio. Now, when you take this ratio of course, here this ordinary differential dp and dv they becomes partial differential why do we say? Because, that point of time we say this equation is true for constant entropy.

$$\frac{c_p}{c_v} = \left[\frac{-\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_v} \right] \left(\frac{\partial p}{\partial v}\right)_s = \frac{\left(\frac{\partial p}{\partial v}\right)_s}{\left(\frac{\partial p}{\partial v}\right)_T}$$

Here, we can see that entire relations between p-v-T and it is a cyclic relations and this term $\frac{-\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_v}$ comes to this expression. Because, p-v-T they are in cyclic, we have used the cyclic mathematical relation.

So, $\left(\frac{\partial p}{\partial v}\right)_s = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{c_p}{c_v}\right)$. Now, we are going to recall the equations $\kappa = -\left(\frac{1}{v}\right) \left(\frac{\partial v}{\partial p}\right)_T$ & $\alpha = -\left(\frac{1}{v}\right) \left(\frac{\partial v}{\partial p}\right)_s$.

So, when you put this equations here $\frac{c_p}{c_v} = \left(-\frac{1}{\alpha v}\right) (-\kappa v) = \frac{\kappa}{\alpha}$.

Again we say for an ideal gas $p = \frac{RT}{v} \Rightarrow \left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{v^2}$; so, this equation we are going to use. Then next target was the how to find another important property what we call as speed of sound. So, speed of sound c is defined from its definition is that it is $c = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}$.

Now, the now $\rho = 1/v$, then the speed of sound is then expressed as $\sqrt{-v^2 \left(\frac{\partial p}{\partial v}\right)_s}$. Now, $\left(\frac{\partial p}{\partial v}\right)_s$ expression you can get from α ; so, we can say $\sqrt{(-v^2) \left(-\frac{1}{\alpha v}\right)}$. So, after simplifying then we can get speed of sound $c = \sqrt{\left(\frac{c_p}{c_v}\right) \left(\frac{v}{\kappa}\right)}$.

And for an ideal gas equations this particular expression further gets simplified by considering this equations : $p = \frac{RT}{v}$ and also $\left(\frac{\partial p}{\partial v}\right)_s = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{c_p}{c_v}\right)$ into $\frac{c_p}{c_v}$, ultimately $c = \sqrt{-v^2 \left(\frac{\partial p}{\partial v}\right)_s} = \sqrt{-v^2 \left(\frac{c_p}{c_v}\right) \left(\frac{\partial p}{\partial v}\right)_T} = \sqrt{\left(\frac{c_p}{c_v}\right) RT}$.

Now, we will move on to next important two equations that is T ds equations and we will find what are its important significance. In fact, when you talk about T ds equations, we already know these equations, but it has to be interpreted in a different form.

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T-ds Equations

- Let us revisit the $T - ds$ equations and establish the mathematical expressions in different forms.
- Two important applications of these equations can be considered: reversible isothermal change of pressure; reversible adiabatic change of pressure.
- **Case I:** At constant temperature (T), the dependence of specific volume (v) and coefficient of volume expansion (β) is insensitive to pressure for solids and liquids.
- It is interesting to note that when the pressure is increases isothermally, heat flows out (for positive β). For substances with negative values of β , (e.g. rubber band, water between 0°C-4°C), the isothermal increase in pressure causes heat absorption.
- The isothermal compressibility (κ) is fairly insensitive to change of pressure and is always a positive quantity. So, the work transfer will be negative due to compression.
- When the pressure is increases isothermally, the internal energy (IE) is increased when heat is absorbed (negative β) and IE drops when heat is liberated (positive β).

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And why we want to go for a different form? Because we are going to apply this equations for two situations; one is reversible isothermal change in the pressure, other is reversible adiabatic change in the pressure. We will see in the first category that is reversible isothermal change in the pressure or at constant temperature we will note down that dependence of specific volume and coefficient of volume expansion is insensitive to pressures for solids and liquids.

Other important point we are going to note that when the pressure increases isothermally heat flows out; that means, heat comes out and for the substances for which beta is positive. Now, for substances with negative value of beta we will see that isothermal increase in the pressure will cause heat absorption.

The other important consequence we will find out is that isothermal compressibility is insensitive to the change in the pressure and it is always a positive quantity. And because of this reason this has linked with respect to work transfer and this work transfer will be negative because it will be a compression situation.

Now, when the pressure increases isothermally, the combined effect of this heat and work, we will have impact on internal energy, This internal energy is going to be increased; now, when heat is absorbed negative beta and internal energy will drop when the heat is liberated. Now, these consequence let us see that how you are going to prove mathematically.

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T-ds Equations

- Effect of reversible isothermal change of pressure for pure substances (Case I)

Recall T-ds Equations: $ds = \frac{c_p}{T} dT + \left(\frac{\partial v}{\partial T}\right)_p dv$ & $ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$

Case I: Reversible isothermal change of pressure

At constant T, $T ds = -T \left(\frac{\partial v}{\partial T}\right)_p dp \Rightarrow Q = -T \int \left(\frac{\partial v}{\partial T}\right)_p dp$

Recall $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$ & $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T$

$\Rightarrow Q = -T \int \beta v dp = -T \beta v \int dp = -T \beta v (p_f - p_i)$

$\Rightarrow Q \approx -T \beta v p_f$ (when $p_i \ll p_f$) ✓

Work transfer, $W = -\int p dv = -\int \left(\frac{\partial v}{\partial p}\right)_T p dp = \int \kappa v p dp = \frac{1}{2} \kappa v (p_f^2 - p_i^2)$

$\Rightarrow W \approx \frac{1}{2} \kappa v p_f^2$ (when $p_i \ll p_f$)

Internal energy, $\Delta E = Q - W$

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So, you can recall this T ds equations; in fact, here we are we will talk about the T ds equations in terms of pressures. So, we say we will use this equation $ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$. Now, reversible isothermal change of pressure will lead to the fact this term will go to 0. So, we can say at constant T we can write this equation as $T ds = -T \left(\frac{\partial v}{\partial T}\right)_p dp$.

So, when you say T ds it refers to heat transfer Q which is $Q = -T \int \left(\frac{\partial v}{\partial T}\right)_p dp$.

Now, this $d\left(\frac{\partial v}{\partial T}\right)_p$ we can find out from the expressions which is β so that we can write this

$Q = -T \int \beta v dp = -T\beta v \int dp$. So, for many substances if you say this Q is a function of dp only; so, $Q = -T\beta v(p_f - p_i)$.

Now, when the final pressure is much higher than the initial pressure, then this expression reduces to a simple one $Q \approx -T\beta v p_f$; now, this is about the heat transfer. Now, for work transfer we have to recall the expression for kappa which we will talk about $W = - \int p dv$; dv information will get from this kappa.

So, now after simplifying this we can write this work transfer $W = - \int p dv = - \int \left(\frac{\partial v}{\partial p}\right)_T p dp = \int_{p_i}^{p_f} \kappa v p dp = \frac{1}{2} \kappa v (p_f^2 - p_i^2)$. Now, when $p_i \ll p_f$; so, we can see what is the work transfer $W \approx \frac{1}{2} \kappa v p_f^2$. So, in the information of Q and W one can find out also internal energy.

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T-ds Equations

Case II: Effect of reversible adiabatic change of pressure for pure substances

- Entropy remains constant in a reversible adiabatic process.
- The increase in pressure causes very negligible change in temperature for solids and liquids. The value of c_p is invariably constant.
- The reversible adiabatic increase in pressure will produce increase of temperature for pure substance (positive β) and decrease in temperature negative values of β .

Recall T-ds Equations: $ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$

Case II: Reversible adiabatic change of pressure

At constant s, $\frac{c_p}{T} dT = \left(\frac{\partial v}{\partial T}\right)_p dp \Rightarrow dT = \frac{T}{c_p} \left(\frac{\partial v}{\partial T}\right)_p dp$

Recall $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$; $\Rightarrow dT = \frac{T\beta v}{c_p} dp$

$\Rightarrow \Delta T = \frac{T\beta v}{c_p} (p_f - p_i)$; $\Delta T \approx \frac{T\beta v}{c_p} p_f$ (when $p_i \ll p_f$)

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The second case, which we are going to study what is the effect of reversible adiabatic change of pressure for pure substance. So, the word reversible adiabatic means it is an isentropic process. So, entropy remains constants and here the inferences that we are going to get is that increase in the pressure will cause very negligible change in the temperature for solids and liquids.

And c_p will be invariably constant, reversible adiabatic change in the pressure will produce increase in the temperature for pure substance, which has positive beta and it decreases in temperature for negative values of beta.

So, here also we recall the same equations $ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$. Now, when I say adiabatic change of pressure; so, entropy becomes 0, ds becomes 0. So, from this expressions we can get $\frac{c_p}{T} dT = \left(\frac{\partial v}{\partial T}\right)_p dp \Rightarrow dT = \frac{T}{c_p} \left(\frac{\partial v}{\partial T}\right)_p dp$. Now, this $\left(\frac{\partial v}{\partial T}\right)_p$ information will get from the value beta.

So, after putting this we get the temperature change when there is a increase in the pressure and this happens at constant entropy. So, the rise in the temperature for the pure substance can be expressed $\Delta T = \frac{T\beta v}{c_p} (p_f - p_i)$. And when $p_i \ll p_f$ we will see that the $\Delta T \approx \frac{T\beta v}{c_p} p_f$.

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Numerical Problems

Q1. The pressure on 2 cm³ mercury at 25°C is increased by 1000 bar in a reversible and isothermal manner. Calculate the amount of heat transfer, work transfer and change in internal energy for the mercury. Take $\beta = 1.8 \times 10^{-4} \text{ K}^{-1}$, $\kappa = 4 \times 10^{-11} \text{ Pa}^{-1}$.

Soln

$Q, W, \Delta E$

$Q = -T \Delta V \beta$

$\Rightarrow Q = (298) (2 \times 10^{-5}) (1.8 \times 10^{-4}) (101325 \times 1000)$

$\Rightarrow Q = -108.7 \text{ J}$ (Heat is absorbed)

$W = -\frac{1}{2} V \kappa \beta^2$

$W = -4.1 \text{ J}$ (done on the system)

$\Delta E = -112.8 \text{ J}$ (Increase in temp)

$T = 25^\circ\text{C} = 298 \text{ K}$

$V = 2 \text{ cm}^3 = 2 \times 10^{-6} \text{ m}^3$

$\beta = 1000 \text{ bar} = (1000 \times 10^5 \text{ Pa}) \times 10^{-2}$

Mercury
2 cm³, T = 25°C

$W (+ve)$
 $Q (+ve)$

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So, this is all about the contents for the lecture today, now based on the content we have discussed we are going to solve some simple numerical problems. And here I say simple because all the expressions has been derived in these previous slides. So, I will note down this expressions directly; so, intendant audience you can please refer the slides for the derivation of the equations.

So, the first problem talks about the last two segment of our discussions; when the pressure is increased in a reversible isothermal manner for a pure substance and when the pressure is increased in the isentropic manner. So, we have a problem that is given we have 2 cm^3 mercury which is available to us as 25 C .

So, you have this mercury in a container and this pressure is increased to 1000 bar. So, final pressure becomes 1000 bar; so, we need to find out through this change in the pressure what happens to Q and what happens to W .

So, first thing we can say that based on our understanding or assumption when work is done by the system it is taken as positive, when heat is added to the system it is also treated as positive. So, for mercury we have the data beta and kappa, what is we need to require? We need to find out Q , W and ΔE . So, this is a case where pressure is increased in a reversible and isothermal manner.

$$Q = -T\beta v p_f = -298 \times (2 \times 10^{-5}) \times (1.8 \times 10^{-4}) \times (101325 \times 1000) = -108.7 \text{ J}$$

And since it is negative, we say that heat is absorbed.

$$W = -\frac{1}{2} \kappa v p_f^2 = -4.1 \text{ J}$$

So, which means work is done on the system that is also true because we are increasing the pressure. And from this we can get $\Delta E = -112.8 \text{ J}$.

So, this means internal energy goes into the systems that is increases, increase in temperature. So, this of course, these numbers Q , ΔE are very small with respect to quantification of increase in the pressure by 1000 bar. So, it means that mercury is very insensitive to these changes; in fact, this is also clear from the values of beta and kappa defined for mercury.

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Numerical Problems

Q2.(a) The pressure on 2 cm³ mercury at 25°C is increased by 1000 bar in a reversible and adiabatic manner. Calculate the change in temperature.

(b) Keeping the volume constant, if the temperature is raised by 10°C, what will be the final pressure? Take the atmospheric pressure as 10⁵ Pa. For mercury, $v = 7.4 \times 10^{-5}$ m³/kg; $c_p = 0.15$ kJ/kg and $\beta = 1.8 \times 10^{-4}$ K⁻¹, $\kappa = 4 \times 10^{-11}$ Pa⁻¹.

$T = 25^\circ\text{C} = 293 \text{ K}$

(a) $\Delta T = \frac{T\beta v}{c_p} \cdot \Delta p$
 $\Rightarrow \Delta T = \frac{298 (7.4 \times 10^{-5}) (1.8 \times 10^{-4})}{0.15} \times 101325$
 $\Rightarrow \Delta T = 2.67 \text{ K}$

(b) $p = p(T, v) \Rightarrow dp = \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial v}\right)_T dv$
 $\Delta p = \frac{\beta}{\kappa} (T_f - T_i)$ $T_i = 293 \text{ K}$
 $\Rightarrow p_f = 452 \text{ bar}$ $\Delta p = p_f - p_i$

Mercury $Q = 0$
 $p_i \rightarrow 1000 \text{ bar}$
 $p_i = 10^5 \text{ Pa}$
 $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$, $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T$
 p, v, T cyclic relation.
 $\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{\kappa}$

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And next problem is in relation with the first problem, but here the association was reversible and adiabatic manner the pressure is increased. So, same mercury we may have this mercury in a container and this container is insulated. So, $Q = 0$ pressure goes to 1000 bar and its initial pressure $p_i = 10^5 \text{ Pa}$ and all other numbers given that specific volume C_p , beta, and kappa; so, we want to find out the change in the temperatures.

So, let us see the first part of the problem,

$$\Delta T = \frac{T\beta v}{c_p} p_f = 298 \times (7.4 \times 10^{-5}) \times (1.8 \times 10^{-4}) \times \frac{(101325 \times 1000)}{0.15} = 2.67 \text{ K}$$

So, we say that mercury is very insensitive to this change in the pressure. Although we have increased the pressure by 1000 bar, but hardly temperature change is recorded as about 2K. And second part again we say that when the volume is kept constant and temperature is raised by 10 C. So, for that we have not derived this relations, which we are going to do now.

$$p = p(T, v); dp = \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial v}\right)_T dv$$

So, here we say keeping volume constant; so, $\left(\frac{\partial p}{\partial v}\right)_T dv$ goes to 0 and this information we require. So, for that we have to recall $\beta = \left(\frac{1}{v}\right) \left(\frac{\partial v}{\partial T}\right)_p$ & $\kappa = -\left(\frac{1}{v}\right) \left(\frac{\partial v}{\partial p}\right)_T$; so, from this

relations we can find out dp . Now, if you say cyclic relation between p , v and T , then from this we can get $\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{\kappa}$; $p_f - p_i = \frac{\beta}{\kappa}(T_f - T_i)$; $p_f = 452 \text{ bar}$.

So, what it says is that if the temperature of mercury is raised by 10 C keeping volume constant, we require 452 bar for this change in the temperature. That is because this value of beta and kappa value is very less; that means mercury is typically insensitive.

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Numerical Problems

Q3. Estimate the percentage of error in c_p for water (1 atm and 20°C) if $c_p = c_v$ is assumed. Also, calculate the speed of sound from specific heat ratio. Take $\rho = 998.2 \text{ kg/m}^3$, $\beta = 0.2 \times 10^{-3} \text{ K}^{-1}$, $\kappa = 49.6 \times 10^{-6} \text{ bar}^{-1}$, $c_p = 4.188 \text{ kJ/kg}$ (at 20°C)

Soln (a) Recall $c_p - c_v = \frac{v T \beta^2}{\kappa}$ At 20°C, $\left\{ \begin{array}{l} \rho = 998 \text{ kg/m}^3 = \frac{1}{v} \\ c_p = 4.188 \text{ kJ/kg} \cdot \text{K} \end{array} \right.$

$$c_p - c_v = \left(\frac{1}{998.2}\right) \frac{(293)(0.2 \times 10^{-3})^2 \times 101.325}{49.6 \times 10^{-6}}$$

$$\Rightarrow c_p - c_v = 0.024 \text{ kJ/kg} \cdot \text{K} \Rightarrow c_v = 4.164 \text{ kJ/kg} \cdot \text{K} \quad \left\| \begin{array}{l} c_p \approx c_v \\ 4.188 \text{ kJ/kg} \cdot \text{K} \end{array} \right.$$

$$\left(\frac{c_p - c_v}{c_p}\right) \times 100 = \frac{0.024}{4.164} \times 100 = 0.5\%$$

(b) $c = \sqrt{\left(\frac{c_p}{c_v}\right) \left(\frac{\kappa}{\rho}\right)}$ $= \sqrt{\left(\frac{4.188}{4.164}\right) \left(\frac{1}{998.2}\right) \times \frac{101.325}{49.6 \times 10^{-6}}}$

$$\Rightarrow c = 1434 \text{ m/s}$$

And the last problem that we are going to discuss is about the relation between C_p and C_v . So, the problem says that what is say the error in C_v for water when we are considering water at one atmosphere and 20 C, if $C_p = C_v$ is assumed. Now, whether this is logical or not; so, this you have to find out.

Second part of this problem is we have to find out this speed of sound as a function of specific heat ratio. So, the relations that we have to recall is first relation $c_p - c_v = v \left(\frac{T\beta^2}{\kappa}\right)$. Now, what we know beta and kappa and at 20 C what we know is $\rho = 998 \text{ m}^3$; $v = \frac{1}{\rho}$.

And also $C_p = 4.188 \text{ kJ/kg}$. Now, when I put this number then we can say

$$c_p - c_v = v \left(\frac{T\beta^2}{\kappa}\right) = \left(\frac{1}{998.2}\right) \left(293 \times (0.2 \times 10^{-3})^2 \times \frac{101.325}{49.6 \times 10^{-6}}\right) = 0.024$$

$$C_v = 4.164 \text{ kJ/kg}$$

So, the question arises that what is the percentage of error in C_v ? So, we can say

$$\frac{C_p - C_v}{C_v} \times 100 = \frac{0.024}{4.164} \times 100 = 0.5\%$$

So, basically if you assume $C_p = C_v$, we will land up in 0.5 percent error. So, it is by default we say $C_p \sim C_v$ and that value is assumed it as a 4.188 kilo joule per kg and this is taken the experimental data which is recorded at constant pressure; so, this is the first part of the problem. Second part of the problem is very simple I have already derived the relations for speed of sound c and $c = \sqrt{\left(\frac{c_p}{c_v}\right) \left(\frac{v}{\kappa}\right)} = \sqrt{(4.188/4.164) \left(\frac{1}{998.2}\right) \frac{101.325}{49.6 \times 10^{-6}}} = 1434 \text{ m/s}$ and that is for the water in the water medium. So, with this I conclude the lecture for the today.

Thank you for your attention.