

## Application of Clausius equation to quasi-static (irreversible) process :

Recall that in the last lecture, we had considered a quasi-static irreversible process for which we can use Clausius equation for change of entropy :

$$dS = \left( \frac{dQ_{in}}{T} \right)_{\text{quasi-static}}$$

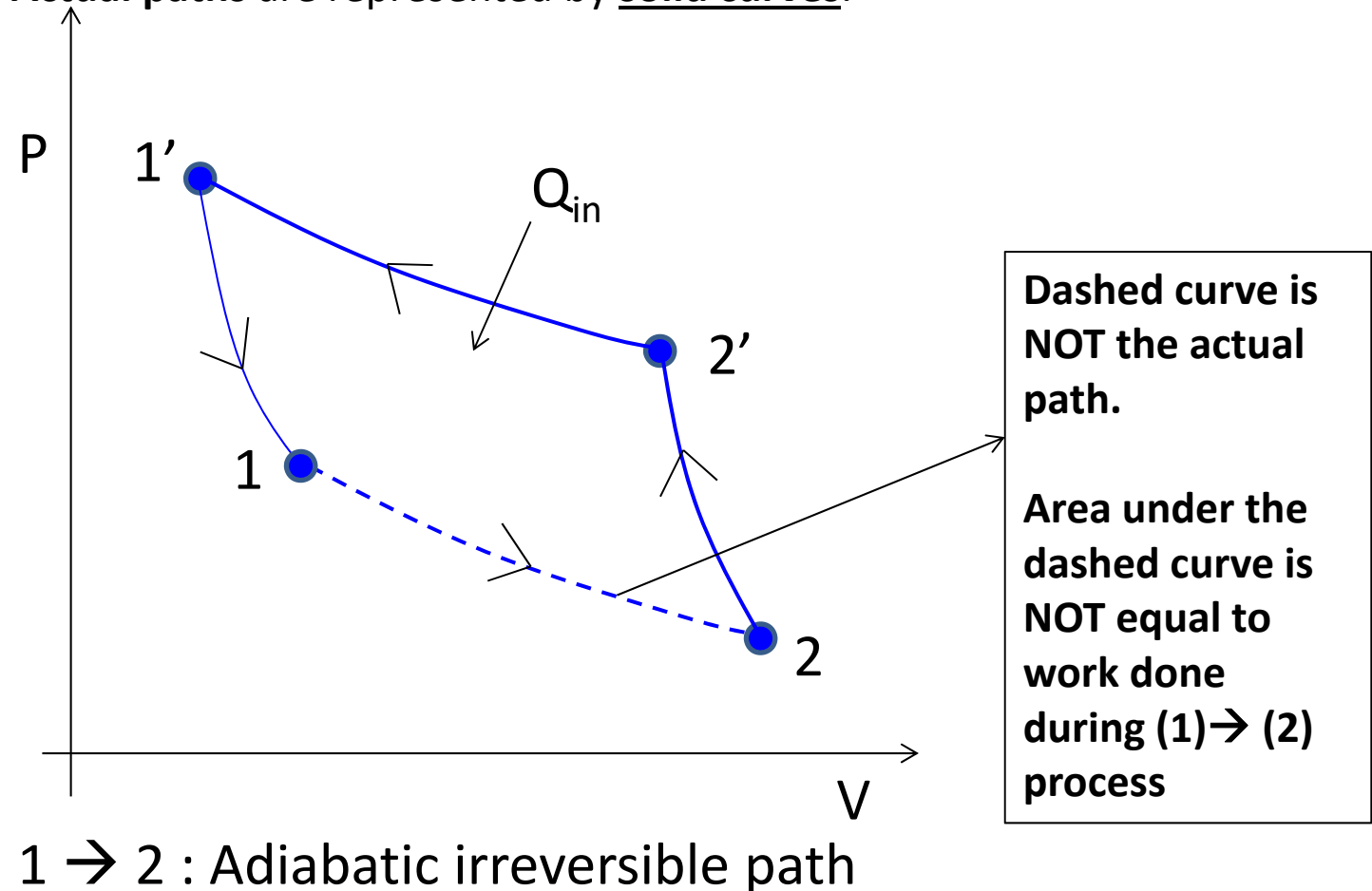
Lets recall the conditions under which we can apply the above equation for a quasi-static irreversible process. The **necessary conditions** for above equation to be applicable are :

The system must be in a state of **internal equilibrium** throughout. This condition implies that (i) internal pressure must be same as external pressure (pressure difference if any is infinitesimal and hence can be neglected) and, (ii) **temperature** must be **uniform** at any given stage of the process. Note that temperature and/or pressure may change during the process.

## Adiabatic irreversible process on a P-V diagram

Recall that in the last lecture, we had considered a cycle in which gas undergoes adiabatic irreversible expansion from (1) to (2) and reversible compression from (2) to (1). The cycle was represented on P-V diagram as shown below.

Note that the **dashed curve** from (1) to (2) is just a representation of the irreversible process. It is **not the actual path**. Area under this dashed curve is NOT equal to the work done in the process. **Actual paths** are represented by **solid curves**.



## Increase of entropy principle

In the last lecture we had discussed statement (5) of second law applicable to adiabatic processes .

Note that if there is no energy transfer in the form of work, then the system can be treated as an isolated system. From statement (5) it follows that :

**The entropy of an isolated system increase in an irreversible (natural) process and remains constant in a reversible process.**

This is also known as “**Increase of entropy principle**”. This is statement (6) of Second law that we have learnt in this course.

## Gibbs equation :

Consider a process between two equilibrium states of a pure substance. Then, the change in internal energy between these states is given by

$$\Delta U = \int_1^2 T \, dS - \int_1^2 P \, dV$$

The important point to note is that this equation only contains quantities that are functions of state. Hence the equation is valid **even if process is not quasi-static or reversible.**

However, the integral over the  $(T \, dS)$  on the right hand side can be equated to heat absorbed in the process **ONLY IF** the process is quasi-static (system is in internal equilibrium and temperature is uniform throughout the process)

Also the integral over  $(P \, dV)$  on the right hand side can be equated to work done by the system **ONLY IF** the process is quasi-static.

## Entropy changes of pure substances :

One can invert Gibbs equation on previous slide to obtain the entropy change between two equilibrium states of a pure substance :

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$\Delta S = \int_1^2 \frac{1}{T}dU + \int_1^2 \frac{P}{T}dV$$

These equations are valid even if the process between the two equilibrium states is irreversible or non quasi-static.

## Enthalpy and entropy changes of pure substances :

One can use Gibbs equation on previous slides to obtain the enthalpy change between two equilibrium states of a pure substance :

$$dH = dU + PdV + V dP$$

Substituting Gibbs equation for  $dU$ , we get

$$dH = T dS + V dP$$

The above equation can be inverted to obtain change in entropy

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

Specific entropy difference between two equilibrium states, can be obtained by dividing the above equation by mass and integrating:

$$s_2 - s_1 = \int_1^2 \frac{1}{T} dh - \int_1^2 \frac{v}{T} dP$$

## How to calculate entropy changes for a pure substance ?

A. Based on the quantity of heat transferred :

(i) If the process also involves transfer of energy in the form of work, change in entropy can be calculated in terms of quantity of heat absorbed using Clausius equality if the process is quasi-static :

$$dS = \left( \frac{dQ_{in}}{T} \right)_{\text{quasi-static}}$$

(ii) If the process does not involve transfer of energy as work (for example if the system is a thermal reservoir), then the process need not be quasi-static or reversible. The change in entropy in terms of quantity of heat absorbed can be calculated by Clausius equality (the only condition is that temperature must be uniform throughout the system)

$$dS = \left( \frac{dQ_{in}}{T} \right)$$

Note that in both cases A(i) and A(ii), the process may be **irreversible** and, in particular, it may involve heat transfer through **finite temperature difference**.

## How to calculate entropy changes for a fixed mass system ?

### B. Based on the thermodynamic relations:

For pure substances and processes in which change of volume is the only Form of work, change of entropy between two states '1' and '2' can be calculated Using either of the following equations

$$s_2 - s_1 = \int_1^2 \frac{1}{T} du + \int_1^2 \frac{P}{T} dv$$

$$s_2 - s_1 = \int_1^2 \frac{1}{T} dh - \int_1^2 \frac{v}{T} dP$$

Note that the above equations are applicable even if the process is **irreversible** or **non quasi-static**.



## Specific entropy changes of ideal gases :

Dividing the expression for the entropy difference (see slide 5) by total mass of the pure substance, we get

$$s_2 - s_1 = \int_1^2 \frac{1}{T} du + \int_1^2 \frac{P}{T} dv$$

As we have learnt in previous lectures, for an ideal gas  $du = C_v dT$

Also, as per ideal gas law,  $P v = R T$

Substituting these relations in the expression for the specific change in entropy, we get

$$s_2 - s_1 = \int_1^2 \frac{C_v}{T} dT + R \ln \left( \frac{v_2}{v_1} \right)$$

Here,  $C_v$  is the specific heat of the ideal gas at constant volume

## Specific entropy changes of ideal gases :

Assuming  $C_v$  to be constant over the temperature range from  $T_1$  to  $T_2$ , the expression on the last slide can be simplified to :

$$s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)$$

If we want to calculate the entropy difference rigorously, i.e., without considering  $C_v$  to be constant, then we make use of ideal gas property tables (Table A-17 to A-24). Table A-17 is partially reproduced below. Here,  $s^\circ$  is the ideal gas entropy, i.e., entropy in the limit of zero pressure or infinite specific volume.

**TABLE A-17**

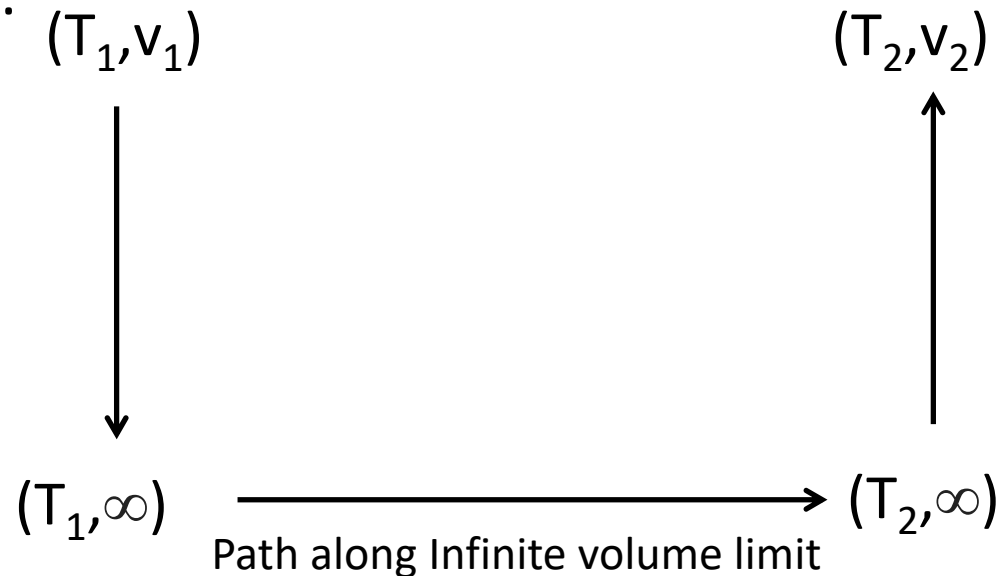
Ideal-gas properties of air

$T$ K	$h$ kJ/kg	$P_r$	$u$ kJ/kg	$v_r$	$s^\circ$ kJ/kg·K
200	199.97	0.3363	142.56	1707.0	1.29559
210	209.97	0.3987	149.69	1512.0	1.34444
220	219.97	0.4690	156.82	1346.0	1.39105
230	230.02	0.5477	164.00	1205.0	1.43557
240	240.02	0.6355	171.13	1084.0	1.47824

## Specific entropy changes of ideal gases :

Making use of Tables A-17 to A-24, we can calculate specific entropy difference as follows:

We consider a path going through states of zero pressure or infinite specific volume.



$$s_2 - s_1 = \int_{v_1}^{v=\infty} \frac{R}{v} dv + \int_{T_1, v=\infty}^{T_2, v=\infty} \frac{C_V}{T} dT + \int_{v=\infty}^{v_2} \frac{R}{v} dv$$

## Specific entropy changes of ideal gases :

Note that in using the path on the previous slide, we have made use of the fact that entropy is a function of state and hence entropy difference between the two states is independent of the path. Combining the first and third integrals in the last equation of previous slide, we get

$$s_2 - s_1 = \int_{T_{1,v=\infty}}^{T_{2,v=\infty}} \frac{C_V}{T} dT + \int_{v_1}^{v_2} \frac{R}{v} dv$$

$$s_2 - s_1 = [s^\circ(T_2) - s^\circ(T_1)] + R \ln \left( \frac{v_2}{v_1} \right) \quad \boxed{\text{III}}$$

Here the entropy values at the infinite volume limit (or zero pressure limit) on the right hand side are obtained from ideal gas property tables (A-17 to A-24)

## Specific entropy changes of ideal gases :

One can also calculate, specific entropy changes of ideal gases using the following relation:

$$s_2 - s_1 = \int_1^2 \frac{1}{T} dh - \int_1^2 \frac{v}{T} dP$$

Substituting  $dh = C_p dT$  and the ideal gas equation of state , we get

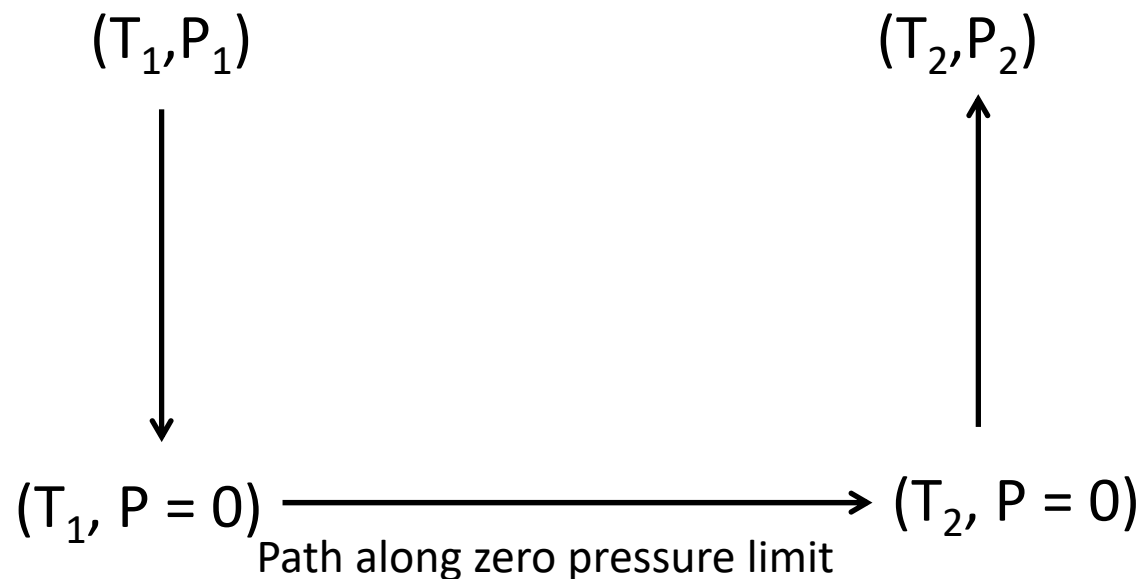
$$s_2 - s_1 = \int_1^2 \frac{C_p}{T} dT - R \ln \left( \frac{P_2}{P_1} \right)$$

If we assume  $C_p$  to be constant, above equation simplifies to :

$$s_2 - s_1 = C_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right)$$

## Specific entropy changes of ideal gases :

If we use a rigorous approach and do not consider  $C_p$  to be constant, we can use ideal gas properties listed in property tables (A-17 to A-24). These ideal gas properties are applicable in the zero pressure limit. We can construct a three step path through zero pressure limit as shown.



Using a method similar to that used previously, we can show that

$$s_2 - s_1 = [s^\circ(T_2) - s^\circ(T_1)] - R \ln \left( \frac{P_2}{P_1} \right)$$

Here the entropy values (in the zero pressure limit) on the right hand side are obtained from ideal gas property tables (A-17 to A-24)

Air is compressed from an initial state of 100 kPa and 17°C to a final state of 600 kPa and 57°C. Determine the entropy change of air during this compression process by using (a) property values from the air table and (b) average specific heats.

**SOLUTION** Air is compressed between two specified states. The entropy change of air is to be determined by using tabulated property values and also by using average specific heats.

(a) The properties of air are given in the air table (Table A–17). Reading  $s^\circ$  values at given temperatures and substituting, we find

$$\begin{aligned} s_2 - s_1 &= s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1} \\ &= [(1.79783 - 1.66802) \text{ kJ/kg}\cdot\text{K}] - (0.287 \text{ kJ/kg}\cdot\text{K}) \ln \frac{600 \text{ kPa}}{100 \text{ kPa}} \\ &= \mathbf{-0.3844 \text{ kJ/kg}\cdot\text{K}} \end{aligned}$$

(b) The entropy change of air during this process can also be determined approximately from Eq. 7–34 by using a  $c_p$  value at the average temperature of 37°C (Table A–2b) and treating it as a constant:

$$\begin{aligned}s_2 - s_1 &= c_{p,\text{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\&= (1.006 \text{ kJ/kg}\cdot\text{K}) \ln \frac{330 \text{ K}}{290 \text{ K}} - (0.287 \text{ kJ/kg}\cdot\text{K}) \ln \frac{600 \text{ kPa}}{100 \text{ kPa}} \\&= \mathbf{-0.3842 \text{ kJ/kg}\cdot\text{K}}\end{aligned}$$