



Chemical Engineering (Thermodynamics I) (UCH305)



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**THAPAR INSTITUTE
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Lecture 21

ENTROPY

(Second Law of Thermodynamics)

Introduction

The second law often leads to expressions that involve inequalities.

$$\eta_{th} \begin{cases} < \eta_{th,rev} \\ = \eta_{th,rev} \end{cases}$$

$$\eta_{th} \leq \eta_{th,rev}$$

Like wise another important inequality that has major consequences in thermodynamics is the **Clausius inequality**.

$$\oint \frac{\delta Q}{T} \leq 0$$

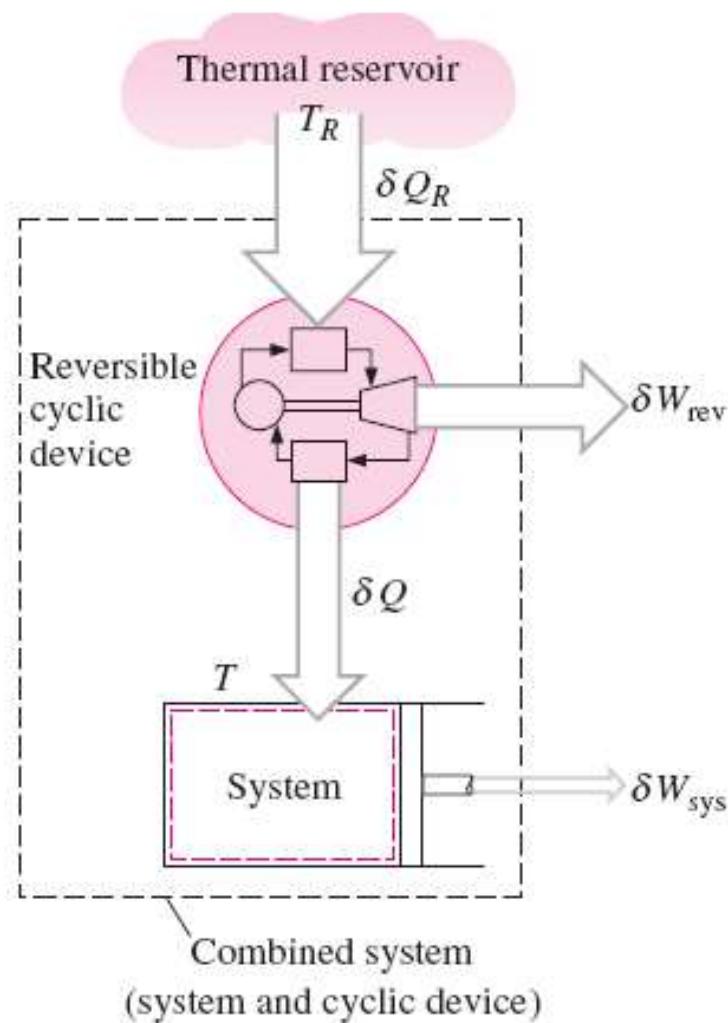
That is, the cyclic integral of $\delta Q/T$ is always less than or equal to zero. This inequality is valid for all cycles, (reversible or irreversible).

Q is the heat transfer to or from the system.

T is the absolute temperature at the boundary.

The inequality of Clausius is a consequence of the second law of thermodynamics.

To demonstrate the validity of the Clausius inequality



Consider a system connected to a thermal energy reservoir at a constant thermodynamic (i.e., absolute) temperature of T_R through a reversible cyclic device (as in fig.)

The cyclic device receives heat δQ_R from the reservoir and rejects heat δQ to the system whose temperature at that part of the boundary is T , while producing work δW_{rev} . The system produces work δW_{sys} as a result of this heat transfer.

The total work of the combined system (δW_C) = $\delta W_{rev} + \delta W_{sys}$

Applying the energy balance to the combined system

$$\delta W_C = \delta Q_R - dE_C$$

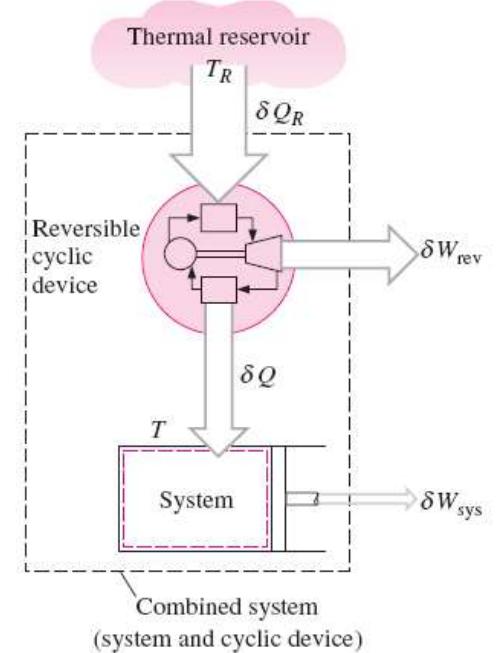
where dE_C is the change in the total energy of the combined system.

Considering that the cyclic device is a *reversible one*,

$$\frac{\delta Q_R}{\delta Q} = \frac{T_R}{T} \longrightarrow \frac{\delta Q_R}{T_R} = \frac{\delta Q}{T}$$

Substituting, we have

$$\delta W_C = T_R \frac{\delta Q}{T} - dE_C$$



Now let the system undergo a **cycle** while the cyclic device undergoes an integral number of cycles.

$$\delta W_C = T_R \frac{\delta Q}{T} - dE_C$$

$$\longrightarrow W_C = T_R \oint \frac{\delta Q}{T}$$

since the cyclic integral of energy (the net change in the energy, which is a property, during a cycle) is zero. Here W_C is the cyclic integral of δW_C , and it represents the net work for the combined cycle.

It appears that the combined system is exchanging heat with a single thermal energy reservoir while involving work W_C during a cycle.

On the basis of the Kelvin–Planck statement of the second law, which states that *no system can produce a net amount of work while operating in a cycle and exchanging heat with a single thermal energy reservoir.*

That is $W_c \neq$ work output and is not a +ve quantity also.

Considering that T_R is the thermodynamic temperature and thus a positive quantity,

$$\oint \frac{\delta Q}{T} \leq 0$$

which is the *Clausius inequality*. This inequality is valid for all thermodynamic cycles, reversible or irreversible, including the refrigeration cycles.

If no irreversibilities occur within the system as well as the reversible cyclic device, then the cycle undergone by the combined system is internally reversible.

As such, it can be reversed. In the reversed cycle case, all the quantities have the same magnitude but the opposite sign.

Therefore, the work W_C which could not be a positive quantity in the regular case, cannot be a negative quantity in the reversed case.

Hence $W_{C,int\ rev} = 0$ since it cannot be a positive or negative quantity, and therefore

$$\oint \left(\frac{\delta Q}{T} \right)_{int\ rev} = 0$$

$$\oint \left(\frac{\delta Q}{T} \right)_{\text{int rev}} = 0$$

Thus, we conclude that *the equality in the Clausius inequality holds good for internally reversible cycles and the inequality for the irreversible ones.*

Here we have a quantity whose cyclic integral is zero.

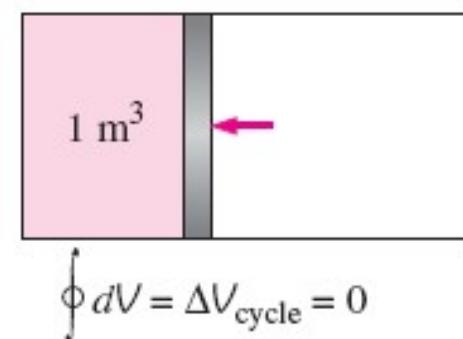
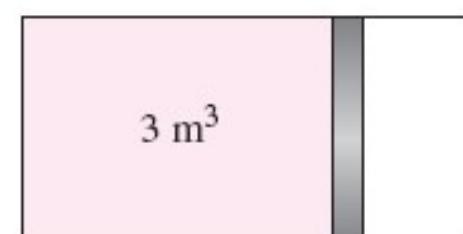
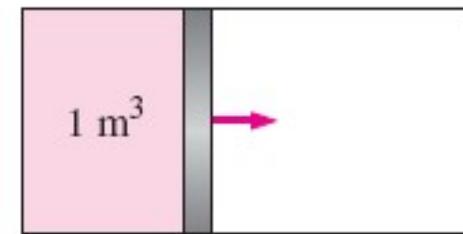
Let us think for a moment what kind of quantities can have this characteristic.

We know that for heat engine the cyclic integral of *work* is *not zero*. Neither is the cyclic integral of heat.
Also work and heat are path functions.

Now consider the volume occupied by a gas in a piston–cylinder device undergoing a cycle. When the piston returns to its initial position at the end of a cycle, the volume of the gas also returns to its initial value.

Thus the net change in volume during a cycle is zero.

$$\oint dV = 0$$



A quantity whose cyclic integral is **zero** depends on the *state only* and not the process path, and thus it is termed as **property**.

Therefore, the quantity $(\delta Q/T)_{int\ rev}$ must represent a property in the differential form.

In 1865, Clausius named this property as entropy.

It is designated **S** and is defined as

$$dS = \left(\frac{\delta Q}{T} \right)_{int\ rev} \quad (\text{kJ/K})$$

Entropy is an extensive property of a system and sometimes is referred to as *total entropy*.

Entropy per unit mass, designated s, is an intensive property and has the unit kJ/kg .

The entropy change of a system during a process can be determined by integrating above equation between the initial and the final states:

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{int\ rev} \quad (\text{kJ/K})$$

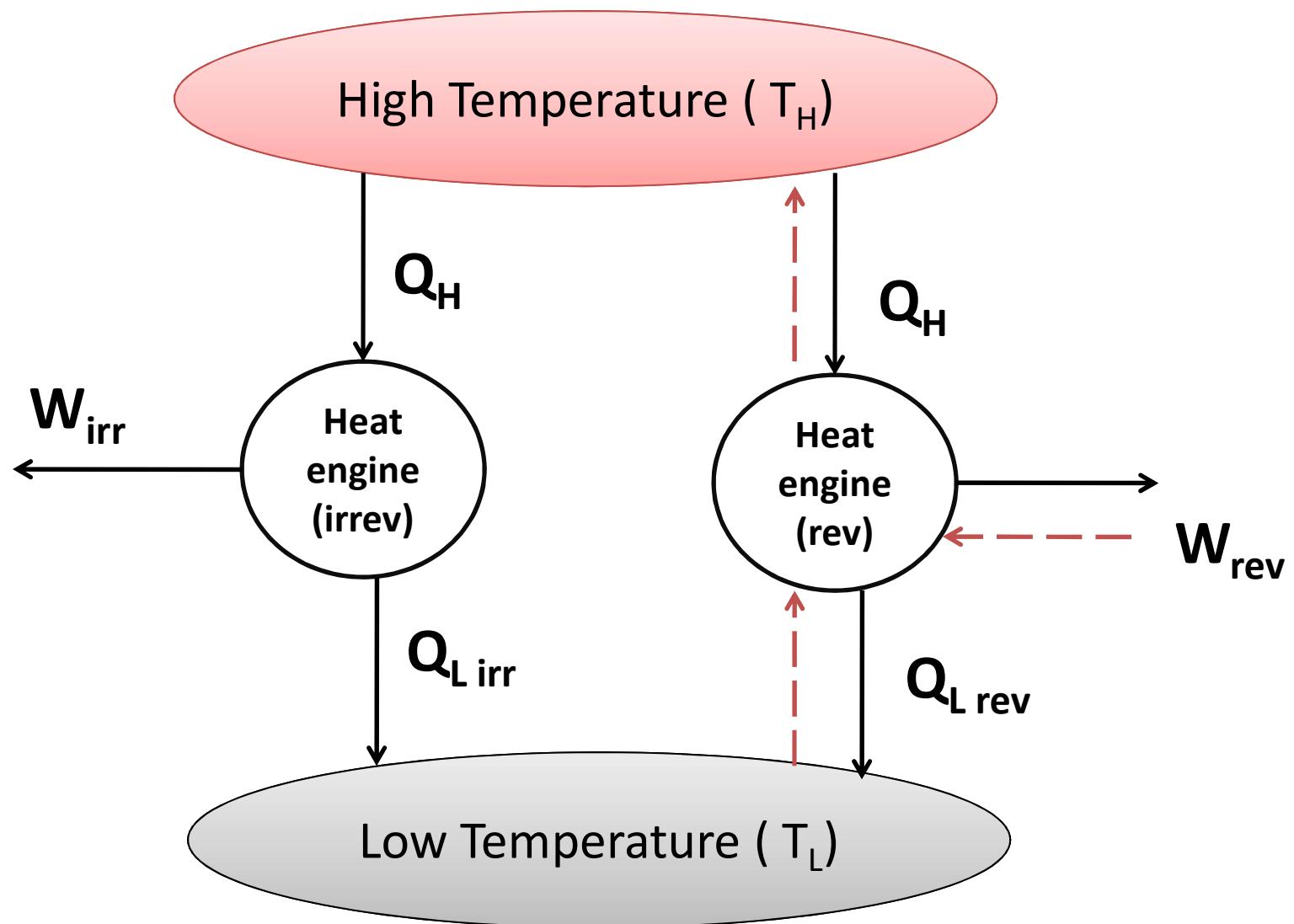
Note that entropy is a property, and like all other properties, it has fixed values at fixed states. Therefore, the **entropy change ΔS** *between two specified states* is the same no matter what path, reversible or irreversible, is followed during a process.

Clausius Inequality

$$\oint \frac{\delta Q}{T} \leq 0$$

This implies the cyclic integral of $\left(\frac{\delta Q}{T}\right)$ always less than or equal to zero.

Let us demonstrate this inequality.



For reversible heat engine

$$\oint \left(\frac{\delta Q}{T} \right)_{\text{rev}} = \int \frac{\delta Q_H}{T_H} - \int \frac{\delta Q_L}{T_L}$$

$$= \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

Since $\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$

Therefore for reversible process

$$\oint \left(\frac{\delta Q}{T} \right)_{\text{rev}} = 0$$

Now for irreversible Heat engine

By Carnot theorem $\eta_{irrev} < \eta_{rev}$

$$W_{irr} < W_{rev} \quad (Q_H - Q_L)_{irr} < (Q_H - Q_L)_{rev}$$

$$Q_H - Q_{Lirr} < Q_H - Q_{Lrev}$$

$$Q_{Lirr} > Q_{Lrev} \quad Q_{Lirrev} = Q_{Lrev} + Q_{diff}$$

$$\oint \left(\frac{\delta Q}{T} \right)_{irrev} = \int \frac{\delta Q_H}{T_H} - \int \frac{\delta Q_{Lrev}}{T_L} = \frac{Q_H}{T_H} - \frac{Q_{Lrev}}{T_L} - \frac{Q_{diff}}{T_L}$$

$$\oint \left(\frac{\delta Q}{T} \right)_{irrev} = -\frac{Q_{diff}}{T_L} < 0 \quad \oint \frac{\delta Q}{T} < 0$$

Hence

For reversible process

$$\oint \left(\frac{\delta Q}{T} \right)_{\text{rev}} = 0$$

And for irreversible process

$$\oint \frac{\delta Q}{T} < 0$$

And combine both we have

“CLAUSIUS INEQUALITY”

$$\oint \frac{\delta Q}{T} \leq 0$$

ENTROPY CHANGE OF PURE SUBSTANCES

Entropy is a property, and thus the value of entropy of a system is fixed once the state of the system is fixed.

The value of entropy at a specified state is determined just like any other property.

In the **saturated mixture** region, it is determined from

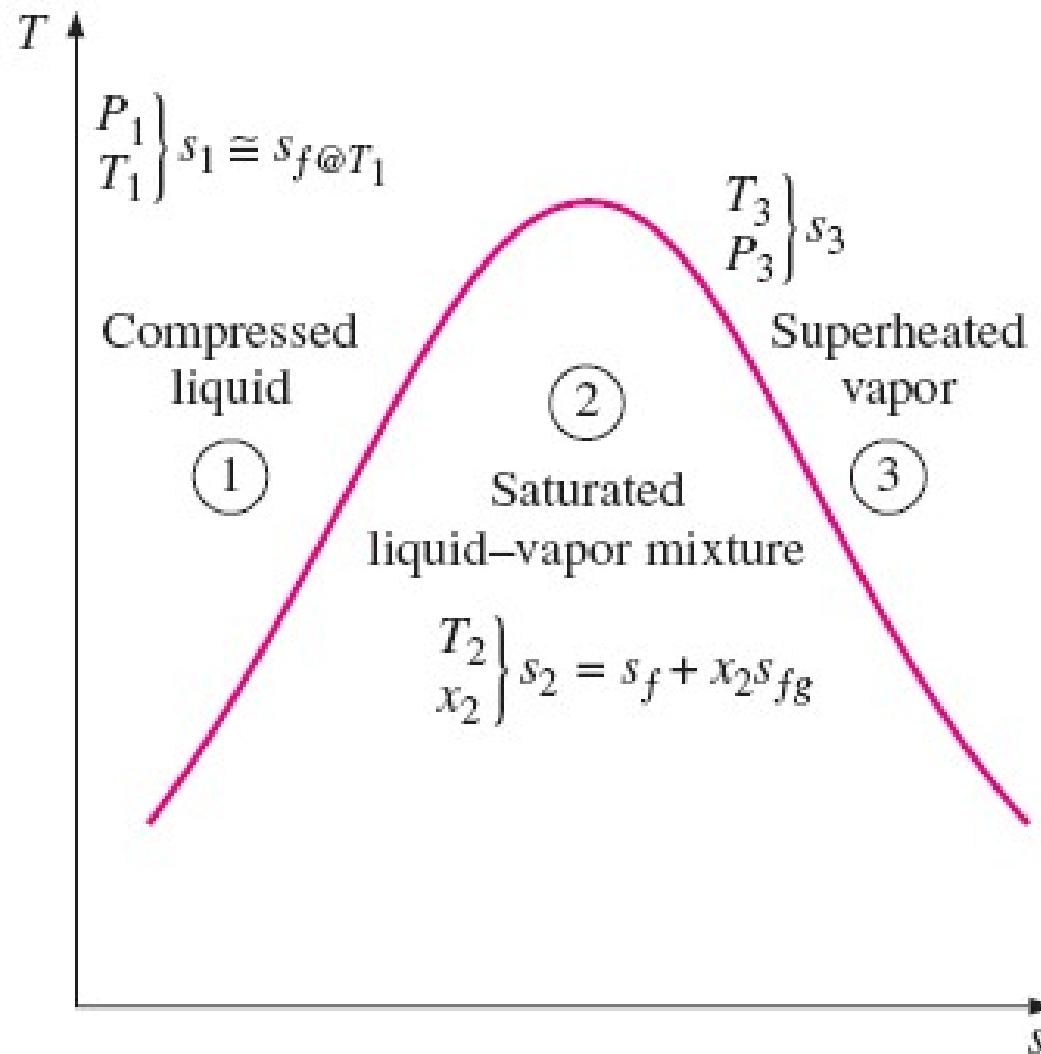
$$s = s_f + x s_{fg}$$

In the absence of **compressed liquid** data, the entropy of the compressed liquid can be approximated by the entropy of the saturated liquid at the given temperature:

$$s_{@ T,P} \equiv s_f @ T \quad (\text{kJ/kg} \cdot \text{K})$$

The entropy change of a specified mass m (*a closed system*) *during a process* is simply

$$\Delta S = m \Delta s = m(s_2 - s_1) \quad (\text{kJ/K})$$



ISENTROPIC PROCESSES

The entropy of a fixed mass can be changed by

(1) heat transfer and (2) irreversibilities

Then it follows that the entropy of a fixed mass does not change during a process that is *internally reversible* and *adiabatic*.

- A process during which the entropy remains constant is called an **isentropic process**.

$$\text{Isentropic process:} \quad \Delta s = 0 \quad \text{or} \quad s_2 = s_1 \quad (\text{kJ/kg} \cdot \text{K})$$

That is, a substance will have the same entropy value at the end of the process as it does at the beginning if the process is carried out in an isentropic manner.

- Many engineering devices (pumps, turbines, nozzles, and diffusers) are essentially adiabatic in their operation, and they perform best when the irreversibilities (such as the friction) associated with the process, are minimized. Therefore, an isentropic process can serve as an appropriate ideal model for actual processes.
- Also, isentropic processes enable to define efficiencies for processes to compare the actual performance of these devices to the performance under idealized conditions.
- It should be recognized that the term *isentropic process* is customarily used in thermodynamics to imply an *internally reversible and adiabatic process*.

$$\delta Q_{\text{int rev}} = T \, dS$$

$$\delta q_{\text{int rev}} = T \, ds$$

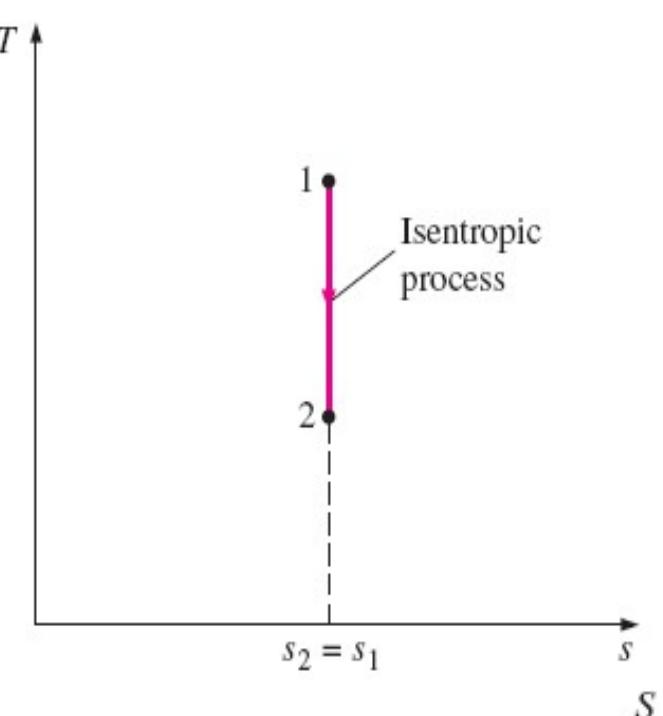
The total heat transfer during an internally reversible process is determined by integration to be:

$$Q_{\text{int rev}} = \int_1^2 T \, dS \quad (\text{kJ})$$

$$q_{\text{int rev}} = \int_1^2 T \, ds \quad (\text{kJ/kg})$$

$$Q_{\text{int rev}} = T_0 \Delta S \quad (\text{kJ})$$

$$q_{\text{int rev}} = T_0 \Delta s \quad (\text{kJ/kg})$$



Therefore, we conclude that *the area under the process curve on a T-S diagram represents heat transfer during an internally reversible process.*

An isentropic process on a T-s diagram is easily recognized as a vertical line segment.

THE $T \ ds$ RELATIONS

The differential form of the conservation of energy equation for a closed system (a fixed mass) containing a simple compressible substance can be expressed for an internally reversible process as:

$$\begin{aligned}\delta Q_{\text{int rev}} &= T \ ds & \delta Q_{\text{int rev}} - \delta W_{\text{int rev,out}} &= dU \\ \delta W_{\text{int rev,out}} &= P \ dV & T \ ds &= dU + P \ dV \quad (\text{kJ})\end{aligned}$$

$$\boxed{\text{or } T \ ds = du + P \ dv \quad (\text{kJ/kg})}$$

This equation is known as the first $T \ ds$, or *Gibbs, equation*.

definition of enthalpy ($h = u + Pv$):

$$\begin{array}{lcl} \longrightarrow & dh = du + P \ dv + v \ dP \\ \longrightarrow & T \ ds = du + P \ dv \end{array} \left. \right\} \boxed{T \ ds = dh - v \ dP}$$

$$ds = \frac{du}{T} + \frac{P dv}{T}$$

and

$$ds = \frac{dh}{T} - \frac{\nu dP}{T}$$

The entropy change during a process can be determined by integrating either of these equations between the initial and the final states.

ENTROPY CHANGE OF LIQUIDS AND SOLIDS

As we know, liquids and solids can be approximated as *incompressible substances* since their specific volumes remain nearly constant during a process.

Thus, $dv \cong 0$ for liquids and solids,

$$ds = \frac{du}{T} = \frac{c \, dT}{T}$$

since $c_p = c_v = c$ and $du = c \, dT$ for incompressible substances.

$$\text{Liquids, solids: } s_2 - s_1 = \int_1^2 c(T) \frac{dT}{T} \equiv c_{\text{avg}} \ln \frac{T_2}{T_1} \quad (\text{kJ/kg} \cdot \text{K})$$

where c_{avg} is the average specific heat of the substance over the given temperature interval.

Note that the entropy change of a truly incompressible substance depends on temperature only and is independent of pressure.

For isentropic processes of liquids and solids T is obtained by setting the entropy change relation above equal to zero. It gives

$$\text{Isentropic: } s_2 - s_1 = c_{\text{avg}} \ln \frac{T_2}{T_1} = 0 \rightarrow T_2 = T_1$$

That is, the *temperature of a truly incompressible substance remains constant during an isentropic process*. Therefore, the isentropic process of an incompressible substance is also isothermal.

THE ENTROPY CHANGE OF IDEAL GASES

$$ds = \frac{du}{T} + \frac{P dv}{T}$$

By substituting $du=c_v dT$ and $P=RT/v$ into this equation ,the differential entropy change of an ideal gas becomes

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

The entropy change for a process is obtained by integrating this relation between the end states:

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

$$ds = \frac{dh}{T} - \frac{v dP}{T}$$

A second relation for the entropy change of an ideal gas is obtained in a similar manner by substituting $dh = c_p dT$ and $v = RT/P$ into this and integrating. The result is

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

Constant Specific Heats

$$s_2 - s_1 = c_{V,\text{avg}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad (\text{kJ/kg} \cdot \text{K})$$

$$s_2 - s_1 = c_{p,\text{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (\text{kJ/kg} \cdot \text{K})$$

Thanks