

Lessione 3-

Recopotional part of Last Lecture since video was lost

If the process is slow so there is always equilibrium
so the work is reversible (ideal):

$$\delta L = -PdV \quad (\text{this is because } \vec{F}_{\text{ext}} = -\vec{F}_{\text{fluid}})$$

In a real process (inversible)

$$\vec{F}_{\text{ext}} = -\vec{F}_{\text{int}} + \vec{F}_w$$

$$\Rightarrow \delta L = \vec{F}_{\text{ext}} d\vec{w} = \underbrace{-\vec{F}_{\text{int}} d\vec{w}}_{-PdV} + \underbrace{\vec{F}_w d\vec{w}}_{\delta L_w}$$

Worked work

We can write:

$$\delta L - \delta L_w = -PdV \rightarrow \begin{array}{l} \text{the reversible work applied} \\ \text{as the work input minus the} \\ \text{waste} \end{array}$$

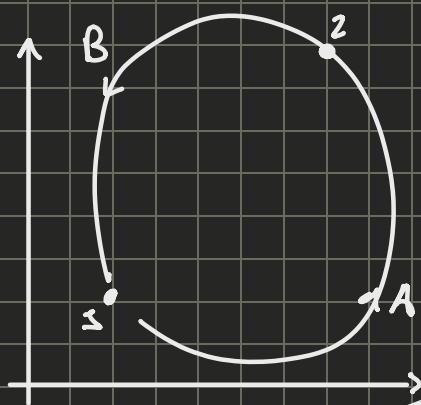
This is the mechanical energy exchanged with fluid.

Absorbing the waste we are no longer looking at thermodynamics of equilibrium states.

Heat Modelling

Heat is the exchange of energy between the fluid and an immobile wall. The exchange of energy causes vibrations of the particles in the wall, heating the wall (or particle). Heat's still a mechanical effect but it's not something we can look like.

In thermodynamic system we can convert heat into work, but it's impossible to entirely convert.



Clausius Theorem Case ideal

$$\oint \frac{\delta Q}{T} \leq 0 \text{ and } \oint \frac{\delta Q}{T} = 0 \iff \begin{matrix} \uparrow \\ \text{MAX HEAT CONVERSION INTO WORK AND TRANS.} \end{matrix}$$

Can only be done through equilibrium states.

$$\oint_{IA} \frac{\delta Q}{T} = \oint_{IB} \frac{\delta Q}{T} = f(1, 2) = \underbrace{S_2 - S_1}_{\text{State function}} = \Delta S$$

Reversible transformations do not exist.

The presence of irreversibility is measured entropy

For any real case in which the process is irreversible

$$\oint \frac{\delta Q}{T} = -\Delta S_{IRR}$$

Case real

If we look at a non cyclic transformation:

$$\int_1^2 \frac{\delta Q}{T} = S_2 - S_1 - \Delta S_{IRR}$$

Contribution
of reversible
process

Just a symbolic nota-
tion, can be
different from one before

$$\Rightarrow \Delta S = \int_1^2 \frac{\delta Q}{T} + \Delta S_{IRR}$$

$$\Rightarrow dS = \frac{\delta Q}{T} + \Delta S_{IRR}$$

Since state
function

Not a state function, since it's
an infinitesimal quantity.

$$\Rightarrow TdS = \delta Q + TS S_{IRR}$$

$$\boxed{\Rightarrow \delta Q = TdS - TS S_{IRR}}$$

Equivalent to law

In a reversible process $S_{IRR} = 0$ (and $\Delta w = 0$)

1st Principle of Thermodynamics:

$$dU = \delta L + \delta Q = -PdV + \delta L_w + TdS - T\delta S_{IRR} \quad \}$$

If the process is irreversible we should write everything,
if it's reversible the δ symbol disappear, but the dU will
remain the same.

dU is the same independent of reversibility, since it's a state
function.

$$dU_r = \delta L_r + \delta Q_r = -PdV + TdS \quad \}$$

For this to be true: $\Rightarrow \delta L_w = TS_{\text{irr}}$

The friction will make a change in entropy, and therefore is irreversible. We can use one to find another.

Fluid machine we want to exchange work and δL_w will be very important.

Since $\delta L_w = TS_{\text{irr}}$

we can always write that $dU = TdS - PdV$

These 5 parameters are the macroscopic trace of all the microscopic effects.

$\Rightarrow U = U(S, V)$ since T and P are:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

So it's still a function of S and V .

	M, U, S
..	
..	
..	
..	
..	
..	
..	

V, U, S are extensive they depend on mass

and P are intensive

To make all the quantities intensive we can define the specific versions of each variable which are intensive

$$u = \frac{U}{M}, \quad s = \frac{S}{M}, \quad v = \frac{V}{M} = \frac{1}{P} \Leftrightarrow P = \frac{M}{V}$$

\hookrightarrow useful in compressible gas machines

We can also write:

$$u = u(s, v)$$

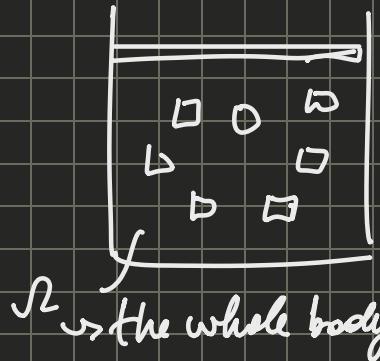
$$T = \left(\frac{\partial u}{\partial s} \right)_{\bar{v}}$$

↓ lower case

$$P = \left(\frac{\partial u}{\partial v} \right)_{\bar{s}}$$

In irreversible processes we look homogeneity, how do we consider this?

11:15



We consider different elements, small enough that each element is homogeneous

\int_2 → the whole body
Each has its own macroscopic properties.

They are big enough to make up the macroscopic properties. This is in between our ideal continuum and the microscopic elements, so we can consider each a thermodynamic system. This means that we can consider our body to be a group of thermodynamic systems. (Postulate of local equilibrium)

U will therefore be valid for the whole body, while u will be valid for each small body. small body we are considering

We can write at the local level

$$\rho = \frac{dM}{dv} = \rho(\vec{x}, t) \rightarrow dM = \rho \cdot dv$$

↓ position

$$\begin{aligned} & \int_2^1 dM \\ & \int_2^1 \rho \cdot dv \\ & \int_2^1 \rho \cdot ds \end{aligned}$$

$$\hookrightarrow M = \int_{\Omega} \rho \cdot dv$$

$$dU = u \cdot dM = \rho u \cdot dv$$

$$\rightarrow U = \int_{\Omega} \rho u \cdot dv$$

$$ds = \partial dM = \rho s \cdot dv$$

$$\rightarrow S = \int_{\Omega} \rho s \cdot dv$$

$U = U(S, V)$ is called Fundamental Relation
due to $u = u(V, S)$ also being valid.

↳ This is valid at all scales, and therefore is valid for
all types of transformations, as well as types of fluid.

We will derive from this the fundamental equation of
thermodynamics

$T = \left(\frac{\partial U}{\partial S}\right)_V$ and $P = \left(\frac{\partial U}{\partial V}\right)_S$ are the equations that
we use to find the thermodynamic relations and to
model our system.

Thermodynamic Potentials

$$H = U + PV \rightarrow h = u + Pv$$

↳ entropy ↳ specific entropy

$$\begin{aligned} dH &= dU + PdV + VdP = TdS + VdP \\ dh &= . - - = TdS + VdP \end{aligned} \quad \begin{cases} H = H(S, P) \\ h = h(S, P) \end{cases}$$

Other thermodynamic potentials are Helmholtz and Gibbs Free energy

$IZ: \infty$

$$U = U(S, V)$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_V}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_S}_{-P} dV$$

$$\left\{ \begin{array}{l} T = \left(\frac{\partial U}{\partial S}\right)_V = T(S, V) \\ P = -\left(\frac{\partial U}{\partial V}\right)_S = P(U, V) \end{array} \right. \quad \begin{matrix} \nearrow \text{equations of} \\ \searrow \text{state} \end{matrix}$$

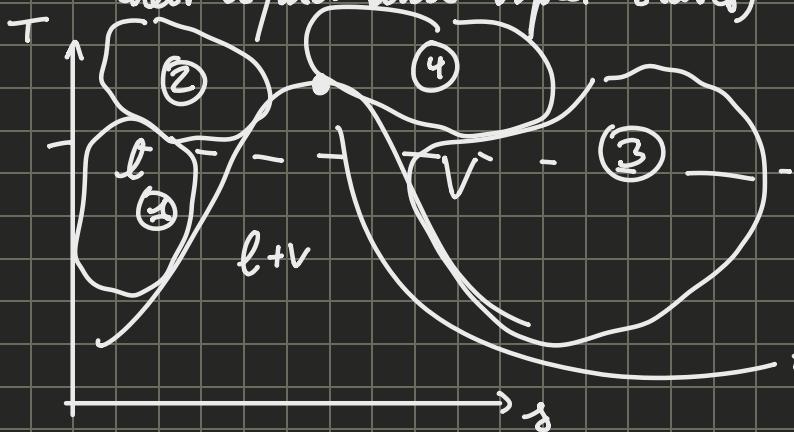
Finding the fundamental
relationship is easier than

Finding the fundamental relationship from V.

If we don't want to use a fundamental relation you need to define two equations of state.

We define these two for every fluid.

In this course we use state diagrams, for different fluids in their liquid and vapor states)



↑ above this there is a change in the system but no net change in state, they are controlled supercritical.

Critical point

① In this area we can use ideal liquid models, they are fluid in which density does not change

② This is the region of the compressible liquid

④ Real gas, vapors in which internal volume forces are not lost.

③ This region can be well represented by the ideal gas (a vapour in which all the particles are points which can have only elastic collisions with no internal volume force).

We will focus on ideal liquids and ideal gases.

Ideal Gases

Note a fundamental relation

$$u = u(T)$$

$$\frac{PV}{M} = \frac{nRT}{M}$$

→ this is a weird equation of state, it's an equation of state because it doesn't say anything on $V = V(S, V)$ so we can say that $T = T(S, V)$

$$[n] = \text{mol}$$

$$M = \text{molar mass} = \frac{\text{kg}}{\text{mol}} \Rightarrow M = n \cdot M$$

so we can have states at equilibrium

$$\Rightarrow P_V = \frac{R}{M} T \Rightarrow P_V = RT$$

$$R = 8314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \rightarrow \text{Air: } M = 28,85 \frac{\text{kg}}{\text{mol}} \Rightarrow R = 287, \dots \frac{\text{J}}{\text{kg} \cdot \text{K}}$$

→ This equation of state tells us the volumetric reaction.

To find this we imagine breaking the fluid.

$$Q \rightarrow q$$

Specific heat

$$Sg \rightarrow dT$$

$C_x \rightarrow$ specific heat, the change in temperature as a function of heat

$$= \left(\frac{\delta q}{\delta T} \right)_x = \cancel{T \frac{ds}{dT}} = T \left(\frac{\partial s}{\partial T} \right)_x$$

There are two specific heats (that are important) with P or V .

Applying heat we assume we are able to perform the process in a reversible way

To deal with the irreversibility of many processes, we usually accept the effects and model an fictional reversible energy exchange which acts like the irreversible process, and therefore allowing us to continue with the reversible hypothesis, like what we have just asked while finding ex.

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$C_P \rightarrow C_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

What's $u = u(T)$?

We know that:

$$du = Tds - Pdv$$

$$\left(\frac{\partial U}{\partial T} \right)_V = \underbrace{T \left(\frac{\partial S}{\partial T} \right)_V}_{C_V} - P \left(\frac{\partial V}{\partial T} \right)_V = C_V = \frac{du}{dT} \rightarrow du = C_V dT$$

↑ since derivative or at constant v
Since C_V is only dependent on T .

For this specific fluid (ideal gases) u does depend on S and V but rather T .

We usually take a reference temperature and a u_{ref}
function:

$$\int_{u_{ref}}^u du = \int_{T_{ref}}^T C_V(T) dT \Rightarrow u = u_{ref} + \int_{T_{ref}}^T C_V(T) dT$$

In an ideal gas

$$h = u + Pv = u(T) + RT = h(T)$$

$$dh = Tds + vdp$$

$$\left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P + v \left(\frac{\partial P}{\partial T}\right)_P^{\circ} = \boxed{C_P = \frac{\partial h}{\partial T}} \rightarrow dh = C_P(T) dT$$

Selecting T_{ref} and h_f $\rightarrow h = h_f + \int_{T_{ref}}^T C_P(T) dT$

We take h_f as the formation enthalpy, the energy at which the chemical reaction occurs.

s on the other hand can be arbitrary.

Entropy of an ideal gas:

$$dh = Tds + v dP \Rightarrow ds = \underbrace{\frac{dh}{T} - \frac{v}{T} dP}_{PV = RT} = \underbrace{\frac{dh}{T} - R \frac{dP}{P}}_{C_P} = \frac{C_P dT}{T} - \frac{R dP}{P}$$

Since s is dependent on both

temperature and pressure, we need to impose a T_{ref} and P_{ref} , as well as S_{ref}

$$s = S_{ref} + \int_{T_{ref}}^T C_P(T) \frac{dT}{T} - R \ln \frac{P}{P_{ref}}$$

These internal models are not what we will use the assumption that C_P and C_V are constant, making our ideal-gas also polytropic.

Ideal diquid

$$\begin{cases} u = u(T) \\ v = \text{const} \end{cases}$$

Purely ideal but simplified the calculation a lot.