

Engineering Thermodynamics

- Definition of Thermodynamics:
 - Thermo : to do with interactions by contact
 - Dynamics: to do with interactions without contact
 - Science of transformation of energy from one form to another and its interaction with matter
 - This course: macroscopic view only: classical thermodynamics:
 - contrast with microscopic or molecular level study:
Statistical thermodynamics: involving kinetic theory and quantum mechanics: not in this course.

History of thermodynamics

- Chronology of thermodynamic laws
 - Second law was enunciated first, by Carnot, in 1820's
 - First law came about fifty years later
 - Third and zeroth laws came another fifty years later
 - Heat and work are distinguished by second law, but taught before first law: many such back and forth definitions: not becoming of a “mother science” such as thermodynamics
- This course:
 - More formal and smooth treatment attempted: no back-and-forth: Follow textbook by P L Dhar

Basic Definitions

- Thermodynamics deals with Objects and their interaction in the presence or absence of contact
- The object needs to be observed in isolation, when no changes are occurring in it spontaneously: “in equilibrium”
 - Object: a part of the world around us that we would like to study
 - Surroundings: Part of the world in the vicinity of the object, which affects / is affected by the object. (not really the rest of the universe!!)
 - Isolation: when there is no form of interaction with other objects or surroundings

Basic Definitions

- Equilibrium: No spontaneous changes occurring in the object during observation, so that correct observation is facilitated
 - eg. a slab with dissimilar temperatures on its two surfaces, if isolated, would have different temperatures for some time, and any measurement in this time period would give erroneous information of the slab temperature
 - Correct temperature obtained when the slab attains uniform temperature throughout: attains thermal equilibrium
 - Different from thermal equilibrium with other objects or surroundings
 - Since all characterization needs equilibrium, we deal with Equilibrium Thermodynamics in this course

Basic Definitions

- An object is characterised by its properties:
 - Property is a macroscopically observable characteristic of an object
 - At any instant there are several properties that characterise an object.
 - Some of these properties are interdependent, and some can be varied independently of the others
 - eg. Mass, volume and density are interdependent
 - Independently variable properties of an object are said to be orthogonal properties

Basic Definitions

- When a system is constituted by many objects, or a system is divided into sub-systems:
 - Properties that remain the same in the sub-systems as that in the original system are called intensive properties: eg: density, pressure, temperature
 - Properties that get divided between sub-systems are called extensive properties: eg: volume, surface area
 - Definition not fundamental: eg: batteries in series / parallel

Basic Definitions

- A combination of properties define the state of an object
 - Thus the state of an object is uniquely defined by a set of all its orthogonal properties.
 - The object is in equilibrium at each of its observable states: equilibrium states
- Change of state of an object from one equilibrium state to another is called a process
- A sequence of processes that return the object to its initial state constitute a cycle

Basic Definitions

- Interaction:
 - When two objects are connected together by a device, they interact
 - Eg: spring-hook, galvanic cell-capacitance connectors, etc.
 - A condition of interaction characterizes the interaction
 - This implies loss of one independent variable.

Basic Definitions

- Generalized Coordinate:
 - A set of independent properties that are orthogonal to each other are called generalized coordinates of an object
 - An object with one mode of interaction has only one generalized coordinate
 - Eg: cylinder-piston (volume) ; battery (charge) etc.
 - An object with many possible modes of interaction has one generalized coordinate for each mode of interaction
 - Eg: capacitor balance

Basic Definitions

- Generalized Force:

- The cause for change in a generalized coordinate during an interaction is the corresponding generalized force:
- Example of spring-spring interaction:
 - If dx' is change in length of one spring and dx'' that of the other, three conditions are possible:

$dx' > 0; dx'' < 0$	$f' < f''$	
$dx' < 0; dx'' > 0$	$f' > f''$	
$dx' = 0; dx'' = 0$	$f' = f''$	(equilibrium)
- In this case, we can identify the spring force as the generalized force. Similar examples: battery; piston

Basic Definitions

- Generalized forces for different interactions:

Interaction

Gen. Force

Gen. Coordinate

Springs

spring force

spring length

Cylinder-Piston

(-)pressure

volume

Battery

voltage

charge

Soap bubble

surface tension

surface area

Magnetic induction

magnetic field

magnetic moment

Basic Definitions

- Interaction by Contact:
 - When two objects are brought in physical contact with each other, the interaction that happens is called “interaction by contact” or “thermal interaction”
 - The result of such interaction:
 - The “warmer” object cools down and
 - The “cooler” object warms up until such time that
 - The two objects are “equally warm”
 - If the empirical “temperature” is the “degree of warmth, then,
 - $T' > T''$ results in cooling of object 1;
 - $T' < T''$ results in warming of object 1;
 - $T' = T''$ results in no interaction; (thermal) equilibrium

Basic Definitions

- Interaction by contact:
 - Generalized force is Temperature (degree of warmth)
 - What is the generalized coordinate?
- Transitivity of Generalized Forces in Equilibrium
$$f' = f''; f'' = f''' \text{ implies } f' = f'''$$
 - Using this rule for temperatures: Zeroth Law
 - $T' = T''; T'' = T''' \text{ implies } T' = T'''$

Generalized Definition of Work

- Work: *“Total effort needed to bring about a desired change”*
 - Valid both in context of daily life, as well as thermodynamics.
 - Thermodynamics: Work is done by an external force, to bring about a change in the object of interest
- In terms of generalized forces and coordinates:

$$W_{\text{on}} = \int f \, dx'$$

– Examples: Spring: $W_{\text{on}} = \int f_2 \, dx_1$;

Battery: $W_{\text{on}} = \int V_2 \, dQ_1$ etc.

Example

20 litres of an ideal gas trapped in a piston-cylinder arrangement at a pressure of 10 bar is expanded isothermally to a final pressure of 1 bar by:

- a) Suddenly reducing the weights over the piston to reduce the external pressure from 10 to 1 bar
- b) Reducing the weights in 2 stages: 10 bar – 8 bar; 8 bar – 1 bar.
- c) Reducing the weights in 3 stages: 10 – 8; 8 – 4; 4 – 1 bar.
- d) Reducing the weights in 4 stages: 10 – 8; 8 – 4; 4 – 2; 2 – 1 bar.
- e) Reducing the weights gradually in a quasi-equilibrium process from 10 to 1 bar.

Compute the work transfer in each case: given $PV = \text{constant}$ for isothermal process in an ideal gas.

Other forms of Work

Extension of a steel rod: $W_{\text{on}} = \int F \, dL$

- Equation of state: Hooke's law; $Y(T)$

Surface tension of droplets: $W_{\text{on}} = \int \sigma \, dA$

Electrical work in charging a battery: $W_{\text{on}} = \int V \, dQ_e$

- Equation of state: Ohm's law; $R(T)$, etc.

Magnetic work in magnetizing a paramagnetic substance: $W_{\text{on}} = \mu_0 \int H \, dM$

- Here μ_0 is the permeability of the medium.

Energy : Adiabatic Work

Joule's Experiment:

When interaction by contact is prevented, the interaction can be called “Adiabatic”

Adiabatic work interactions between same initial and final states: Same amount of work done: independent of path, kind of interaction (electric, mechanical, etc.)

Energy

$W_{\text{on,ad}}$ depends only on the initial and final states

This can then be written as the change of a state function (property) E of the object

$$E_f - E_i = W_{\text{on,ad}}$$

E can be called “energy” of the object

Consistency with classically known “energy”

- Raising an object: Potential energy
- Accelerating an object: kinetic energy
- Electrically charging an object: Electrical energy
etc.

Heat and First Law

When the interaction is not adiabatic, ie, interaction by contact is permitted, then the work is not equal to adiabatic work:

$$W_{\text{on}} \neq W_{\text{on,ad}} : \quad W_{\text{on}} = W_{\text{on,ad}} + Q_{\text{out}} - Q_{\text{in}} = W_{\text{on,ad}} - Q_{\text{in}}$$

$$Q_{\text{in}} = W_{\text{on,ad}} - W_{\text{on}}$$

Caratheodory (1909): First Law of Thermodynamics

$$W_{\text{on,ad}} = E_f - E_i = W_{\text{on}} + Q_{\text{in}} = Q_{\text{in}} - W_{\text{by}}$$

Heat

Consistency with classical understanding

Example of isolated pair of objects interacting thermally

$$E_i' + E_i'' = E_f' + E_f''$$

Rearranging gives $Q_{in}' = -Q_{in}''$

- This is our classical understanding of heat transfer

First Law statements

For a process:

$$E_f - E_i = W_{on} + Q_{in}$$

For a cycle: Change in energy for the processes adds up to zero:

$$\sum W_{on} + \sum Q_{in} = 0$$

$\sum W_{on} > 0$: Refrigeration cycle : $\sum Q_{in} < 0$: use of work to pump heat from lower temperature to higher temperature.

$\sum W_{on} < 0$ or $\sum W_{by} > 0$: Power Cycle: converting the heat supply into work output.

Energy as a property

Defined as: the capacity to do work.

Units: same as work: J

Reference state where energy = 0: arbitrary choice

Adiabatic work of all kinds constitute change in energy: Electrical, Magnetic, elastic, compression, etc.

Storage of energy in an object:

- Intrinsic: Molecular translation, rotation, vibration, electronic motion, nuclear, etc: Internal energy
- Extrinsic / Macroscopic: Potential, Kinetic
- **$E = U + PE + KE$; U: Internal**

Heat Vs Work

Electricity: treated as work;

Frictional dissipation: work done on the interface;
internal energy of interface increases.

Examples: air resistance; friction between solids

Adiabatic Accessibility

Between two given states I and F,

$$E_f - E_i = W_{\text{on,ad}}$$

But can F be reached from I adiabatically?

- When there are no restrictions, all states are accessible from any other state.
- Not always possible when restrictions are imposed, eg, adiabatic

- We then use $E_i - E_f = -W_{\text{on,ad}}$

How to know which states are accessible?

- Examples: Electric work, compression work

Electric work interaction

Adiabatically accessible states from an initial state I:

First consider constant energy, adiabatic processes:

- Insulated battery (adiabatic)
- At constant energy, we can at best decrease charge by short circuiting
- Any attempt to increase charge would increase energy as well.

If energy is allowed to change:

- If we increase charge, E also increases (decreasing E states not accessible adiabatically)
- If we decrease charge, E also decreases (increasing E states not accessible adiabatically)

Compression work interaction

Adiabatically accessible states from an initial state I:

First consider constant energy, adiabatic processes:

- Insulated cylinder-piston (adiabatic)
- At constant energy, we can at best increase volume by free expansion against vacuum
- Any attempt to decrease volume would increase the energy (not possible by constant energy adiabatic process)

If energy is allowed to change:

- If we increase volume, E decreases (increasing E states not accessible adiabatically)
- If we decrease charge, E also decreases (decreasing E states not accessible adiabatically)

Second Law of Thermodynamics

Caratheodory, 1909:

In the neighbourhood of any initial state, there exist states that are not accessible adiabatically.

Reversible process:

Any process which can be retraced backwards to its initial state, restoring both the object and the surroundings to their initial states, is called a Reversible Process

- In context of the examples:
 - States accessible adiabatically and reversibly
 - States accessible adiabatically but only irreversibly
 - States not accessible at all adiabatically

Second Law

Stated more elaborately,

In the neighbourhood of any initial state, there exist

- States that are accessible adiabatically and reversibly
- States that are accessible adiabatically but only irreversibly
- States not accessible adiabatically at all

This is the statement of the second law of thermodynamics, following Caratheodory (1909)

Reversible / Irreversible Processes

A process is reversible when

The departure from equilibrium is always infinitesimal throughout the process. : Quasi-equilibrium process

Irreversibilities are owing to

Finite departure from equilibrium

- Heat transfer across a finite temperature difference
- Charge / discharge across a finite voltage difference ...

Friction, electrical resistance, any dissipation process

Thus, all natural processes are irreversible

- Reversible process is an ideal for reference, can at best be approached, not achieved.