CHE260

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Contents

1   Efficiency and Entropy

the equation for efficiency is defined as:

$$eff\% = \frac{W}{Q_H}$$

where W = work output and Q_H = heat input
Another important concet is entropy defined as

$$\delta s = \frac{Q}{T}$$

Q is the heat transfered and T is the temperature of the system
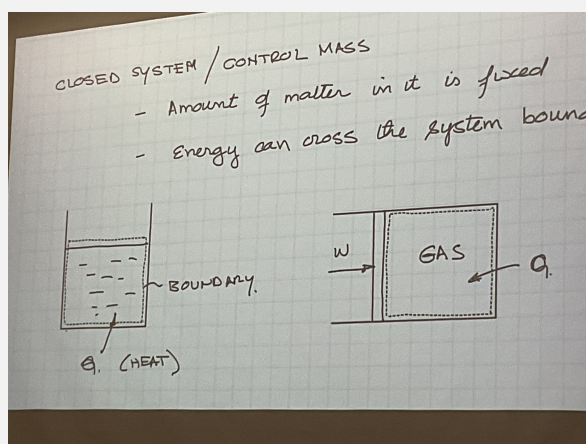
2   Definition of Systems

Here are a few definitions that are helpful for the understanding of thermodynamics:

- System: Any piece of molten on region of space that is defined by a boundary, or the region that we focus.

The most important system we will be using is a **Closed System / Controlled Mass** defined by:

- Amount of matter is fixed inside

- energy can cross the system boundary input or output

- Boundary can also be shifting.

Example 1: an example of a closed system is a piston where gas is limited in the cylinder although the boundary is shifting overtime with energy input.

the image above gives the example of a closed piston system

on the contrary we have **Open System**:

- Both mass and energy can cross system boundary

a few more definition of terms include:

> **Definition: Property**
> Any attribute of a system that can b measured without knowing the history of the system.

Now lets move into some classical mechanics

2.1   Work

suppose you move a block for a infinitestimal distance dx, the total displacement would be

$$\Delta x = \int_{x_1}^{x_2} dx = x_2 - x_1$$

for an infinitestimal amount of work δW would be:

$$\delta W = F dx$$

which is equivalent to:

$$W_{12} = \int_{x_1}^{x_2} F dx$$

2.2 Heat

another form of energy would be Heat:

> **Definition**: **Heat**
> a form of thermal energy that represent the change in temperature

Yet, Heat is not a property, it is similar to Work; an energy change δQ

2.3 Mass

to denote the change in mass of a system we use Δm

Yet properties are also divided into parts:

- Intensive: specified at a point in the system - do not depend on the mass of the system (i.e. Temperature)

- Extensive: depend on the mass of the system(i.e. m,V,E)

The way to convert any extensive property to an intensive property by dividing by mass:

> **Example 2:**
>
> $$\sigma = \frac{V}{m} [\frac{m^3}{kg}]$$
>
> which represents the specific volume of the system or inverse of the density of the system.

> **Definition**: **SteadyState**
> it is defined as the properties in the system do not change with time and remain constant mass while the system is interacting with surroundings.

Another simular state is:

> **Definition**: **Equilibrium**
> Define for **Isolated System**: no mass or energy left the system boundary. such that there is no net transfer of energy.

what this equilibrium implies are:

- Uniform distribution of energy / temperature

- Property can only be defined at equilibrium

Quasi-equilibrium Process can be reached by measuring equilibrium pressure at every small change in piston displacement.
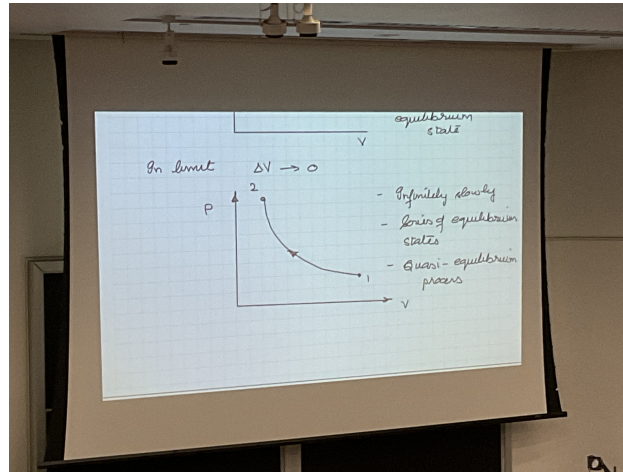
3 Pressure vs. Volumn

Figure 1: image of the pressure volume curve

the image above shows the quasi-equilibrium process which

- use the least amount of works required to compress the gas

> **Definition**: **Idealized Process**
> The idealized process is the process that yields the least amount of work to compress the gas

NOw the question is how do we get a relation bewteen pressure, volume, and temperature and we do this via **Ideal Gas Equation**:

$$PV = nRT$$

where P is pressure, V is volume, n is the # of moles, R is the universal Gas constant $(8.34kJ/kmol)$ and T stands for temperature in Kelvin.

Example 3: A spherical ballon with diameter 6m is filled with helium at 20C and 200kPa. Determine the number of moles in this ballon.
Answer:

$$PV = nRT$$
$$n = \frac{PV}{RT}$$

we sub in the volume obtained by calulating the volume using the diameter and we eventually obtain the following equation:

$$n = \frac{200 * 100^3 Pa * 113.1m^3}{8.314 * 10^3 * (273 + 20)}$$

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the formal definition of an ideal gas is:

- All molecules move randomly

- All have the same mass

- Collide Elastically

- molecules are point masses(no spin)

- No long-range Interaction

Now lets move on to how an ideal gas bahave in a cavity: lets say we have a molecule hitting the wall at velocity v and bounce back with -v of mass m, the change in momentum is:

$$\Delta p = -2mv$$

which is negative to the change in momentum of the wall. Yet the distance travelled between the walls is 2L, so the time bewteen collisions is:

$$t_collision = \frac{2L}{v}$$

and force on wall becomes:

$$\frac{2mv}{2L/v} = \frac{mv^2}{L}$$

and the pressure on the wall also becomes:

$$\frac{mv^2}{L}(\frac{1}{L^2})$$

and the pressure caused by one molecule is then:

$$\frac{mv^2}{L^3}$$

from this we can introduced the idea of a root mean squared velocity of each molecules:

$$v^2_{rms} = 3v^2_x$$

$$P = 1/3\frac{v^2_{rms}}{L^3}m$$

$$PV = \frac{1}{3}mv^2_{rms} = nRT$$

by rearranging the equations we get the following expression for the root mean square:

$$\frac{1}{2} * \frac{M}{N_a}v^2_{rms} = \frac{3}{2}\frac{R_u}{N_a}T$$

which is the kinetic energy of one molecule, and by multiplying both sides by N we can find the total energy of the system so called **Internal Energy**:

$$U = \frac{3}{2}NR_uT$$

So what are some forms of **Energy** in this case:

- Microscopic: change in position on velocity of system

- Macroscopic: Change in temperature or pressure

and all these sum to the formal definition of **Internal Energy** which is

> **Definition**: **Internal Energy**
> any molecular forms of energy, molecule velocity, molecule spin, molecular vibration, or chemical bonds

and the total energy would be:

$$\text{Total Energy} = Ke + Pe + U \tag{1}$$

Example 4: if we have a monoatomic gas the change in internal energy is:

$$U_2 - U_1 = \frac{3}{2}NR_u(T_2 - T_1)$$
$$\Delta U = \frac{3}{2}mR(T_2 - T_1)$$

4   Boundary Work

for a system of piston, the work is defined as follow:

$$w_{12} = -\int_{V_1}^{V_2} P(V)dV$$

and it can be categorized into 2 situations:

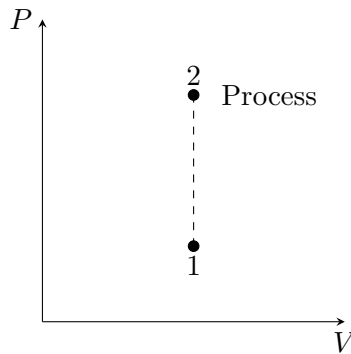- Compression: $dV < 0$ $w_{12} > 0$
- Expansion: $dV > 0$, $w_{12} < 0$

if the work is positive meaning the environment is doing work to the system.

Isochoric Process

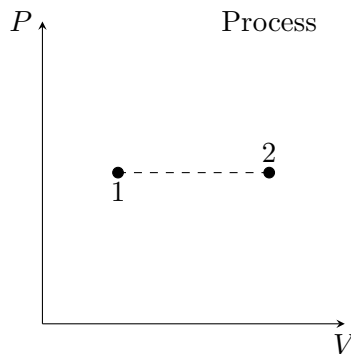THe first special condition is a "constant volume" condition such that:

- Work $= 0$

and the P-V graph would look like this:

Isobaric Process

The second condition would be a "constant pressure condition" and the graph look like this

and the work of the system can be calculated as:

$$w_{12} = -\int_{V_1}^{V_2} PdV = -P\int_{V_1}^{V_2} dV$$
$$w_{12} = -P(V_2 - V_1)$$

Isothermal process

the third condition is a constant temperature process, defined by

$$PV = nRT$$

which tells that the ratio bewteen PV is a constant. and we can calculate the work as:
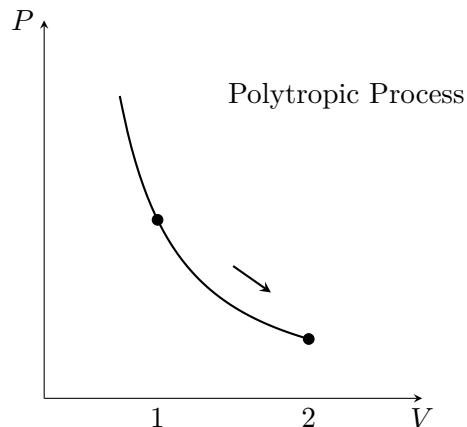
$$w_{12} = -\int_{V_1}^{V_2} PdV$$
$$w_{12} = -nRT\int_{V_1}^{V_2} 1/V\,dV$$
$$w_{12} = -nRTln(\frac{V_2}{V_1})$$

Polytropic Process

a special process is called a polytropic process where the P V diagram is:

and an assumption we have is:
$$PV^n = C$$

and the work can then be calculated by:

$$w_{12} = -\int_{V_1}^{V_2} PdV$$
$$w_{12} = -C\int_{V_1}^{V_2} V^{-n}dV$$
$$w_{12} = \frac{P_2V_2 - P_1V_1}{n - 1}$$

Definition: **Enthalpy**

it is defined by:
$$H = U + PV$$

and the unit is [J], where U is the internal energy

5   Energy Balance

Constant Pressure

the change in energy of a system can be described by:

$$\Delta U = Q + W$$

yet by taking an expansion for U and W:

$$Q_{12} = (U_2 - U_1) + (P_2 V_2 - P_1 V_1)$$
$$Q_{12} = (H_2 - H_1)$$

therefore, the conclusion is that for a **constant pressure process**, the heat added is **the change in enthalpy**

Constant Volume

for a constant volume system the work $W_{12} = 0$ so all the change in energy would be from the heat added to the system.

$$Q_{12} = U_2 - U_1$$

Specific Heat
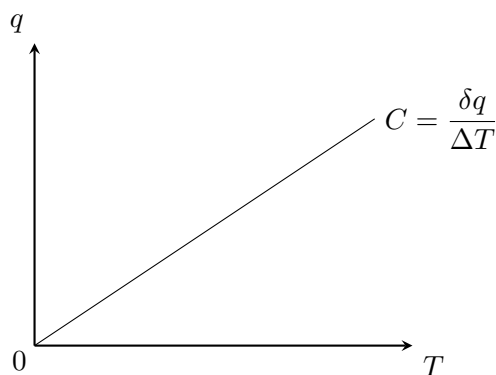
> **Definition**: **Specific Heat**
> The amount of energy needed to raise the temperature of a unit mass of a substrance by 1 degree

and the specific heat C_{avg} is equivalent to:

$$C_{avg} = \frac{Q}{m\Delta T} = \frac{q}{\Delta T}$$

and if we write C as a function of temperature

$$C(T) = \frac{\delta q}{dT}$$

and for a constant volume the situation in a closed system where δW is 0

$$\delta q = dU$$

now suppose the system is open with constant pressure.

$$\delta q + \delta W = dU$$

$$\delta q = dU + PdV$$

some interesting observation can be seen if we take a differential to the enthalpy definition:

$$h = U + PV$$
$$dh = dU + PdV + VdP$$
$$\delta q = dh$$

now lets bring the conclusion to the definition of specific heat.

- Constant Volume:
$$C_V(T) = \frac{\partial U}{\partial T}_V$$

- Constant Pressure:
$$C_P(T) = \frac{\partial h}{\partial T}_P$$

now lets bring the topic back to ideal gas. from previous lectures we've learned a bit more about the energy of the system such that U is only a function of **temperature** and PV is just a function of **RT** therefore

Idea: the equation of **Enthalpy** can be rewritten in the form of T dependent only

$$C_V = \frac{dU}{dT}$$
$$C_P = \frac{dh}{dT}$$
$$\frac{dh}{dT} = \frac{dU}{dT} + R$$

which is equivalent to:

$$C_P = C_V + R$$

and an important definition is the specific heat ratio:

Definition: **Specific Heat ratio** is defined by

$$\gamma = \frac{C_P}{C_V}$$

which would be important for various calculation of heat process

and now we can find a simpler definition for the change in energy.

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

$$\Delta h = \int_{T_1}^{T_2} C_P dT$$

Example 5: Air is heated from 300K to 400K, for air

$$C_v = 0.717 \frac{KJ}{kgK}$$

$$C_P = 104$$

and we can calculate the change in energy of the system

$$\Delta U = 0.717(400 - 300) = 71.7 \frac{KJ}{kg}$$

$$\Delta h = 100.4 \frac{KJ}{kg}$$

if in a process we go from T_1 to T_2, then the average temperature

$$T_{avg} = \frac{T_2 - T_1}{2}$$

can evaluate C_P and C_V using the chart attached for this course. and there are some asuption that would carry over throughout the course for solids and liquids:

- Incompressible Substances

- Cannot do boundary work yields $C_V = C_P$ aka no external work done

another equation to note is:

$$\Delta h = c(T_2 - T_1) + V(P_2 - P_1)$$

6 Lecture 8 Second Law of Thermodynamics

there are a few ways for engine to ouput work to external system

- to increase amount of work $=>$ increase T_H

- in limit $T_H => T_C$ there is no work done since the efficiency is 0.

In reality, the higher the temperature the more work we can get. And yet,the parameter we use to define the quality of energy is **Entropy**.

> **Definition**: **Entropy**
> extensive property that changes when **Heat** is added or removed from a system. Defined by the equation.
> $$\text{Entropy} = \frac{\text{Heat added}}{\text{Temperature}}$$
> which is equivalent to:
> $$S_2 - S_1 = \Delta S = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T}$$

so now lets discuss a few conditions for the equations:

Isotermal condition

The equation for entropy is then defined as:

$$\Delta S = \frac{Q_{12}}{T}$$

since T is a constant. and now lets describe a complete thermal cycle, When converting from state A with temperature $T + \Delta T$ to state B with temperature T with heat transfer of Q bewteen the states the entropy in both states is defined by:

$$|\Delta S_A| = \frac{Q}{T + \Delta T}$$
$$|\Delta S_B| = \frac{Q}{T}$$

and the change in entropy, or the entropy generated is the difference between B and A which is not 0. therefore a conclusion we can have is:

> **Idea**: There is entropy generated when heat transfer occurs between two systesm whose temperature differes by a finite amount

and now we can introduce the second law of tehermal dynamics:

> **Definition**: **Second law of Thermodynamics**
> The entropy of an isolated system wil increase until the system reaches an equilibrium. The

entropy of an isolated system in equilibrium stays constant.

$$dS_{isolated} > 0 \text{not in equilibrium}$$
$$dS_{isolated} = 0 \text{equilibrium}$$
$$dS_{isolated} < 0 \text{not possible}$$

entropy is the measure of unefficiency