Lecture 2
Entropy and Second Law

Etymology: *Entropy, entropie in German.*
En from energy and trope – turning toward
Turning to energy

Zeroth law – temperature
First law – energy
Second law - entropy

Lectures of T. Pradeep

Motivation for a "Second Law"!!

First law allows us to calculate the energy changes in processes.
But these changes do not suggest spontaneity. Examples: H, U.

Distinction between spontaneous and non-spontaneous come in the form of Second law:

Kelvin's statement: "No process is possible in which the sole result is the absorption of heat from the reservoir and its complete conversion to work".

Compare with first law….complete process
Spontaneous process has to transfer part of the energy.

Entropy – measures the energy lost

Second law in terms of entropy: Entropy of an isolated system increases in the course of a spontaneous change:
$$\Delta S_{tot} > 0$$

For this we need to show that entropy is a state function

Definition:
$$dS = dq_{rev}/T$$

For a change between i and f:

$$\Delta S = \int_i^f dq_{rev}/T$$

Choose a reversible path for all processes.

$q_{rev} = -w_{rev}$

Wrev is different from w
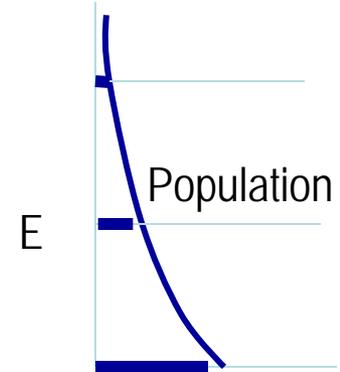
$$\Delta S = q_{rev}/T = 1/T \int_i^f dq_{rev} = nR\ln V_f/V_i$$

$$ds_{sur} = dq_{sur,rev}/T_{sur} = dq_{sur}/T_{sur}$$

Adiabatic, $\Delta S_{sur} = 0$

Statistical meaning of entropy

E   Population

Molecules can possess only certain number of energy states.

They are distributed in energy levels. Population refers to the average number of molecules in a given state. This can be measured.

As temperature increases, populations change. Number of molecules, N_i found in a given state with energy E_i, when the system is at thermal equilibrium at T is,

$$S = k \ln W$$

$$N_i = Ne^{-E_i/kT}/\sum e^{-E_i/kT}$$

W – number of microstates
W = 1, S = 0

Entropy as a state function

Carnot's cycle or Carnot cycle shows that.

Concept: Engine is a cycle

Sadi Carnot

French Physicist: 1796 – 1832
1824 $\rightarrow$ The book, " On the motive power of fire"
First definition of work
 "Weight lifted through a height"
Coriolis generalised it to " force acting through a distance against resistance".
Died by Cholera at the age of 36.
His law was generalised by Clausius.

Heat

Engine

Heat

Work

In the Carnot engine (cycle), a heat engine is made
to do work between temperatures T_h and T_c.
In an **isothermal reversible expansion** of an ideal gas,
$\Delta U = 0$ and $q = -W$.
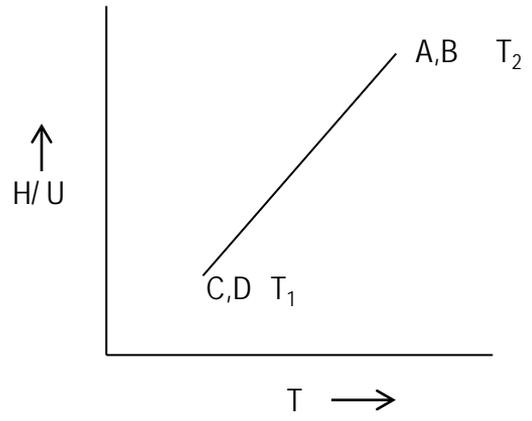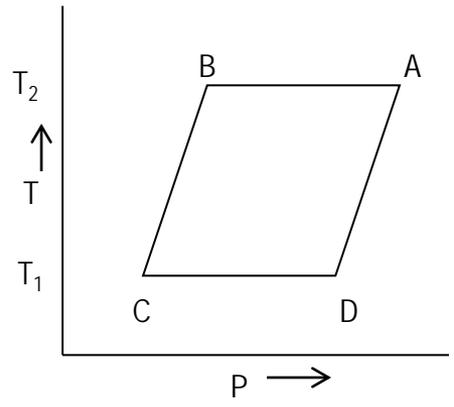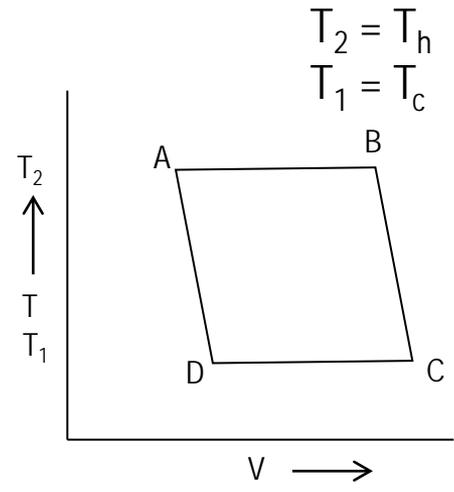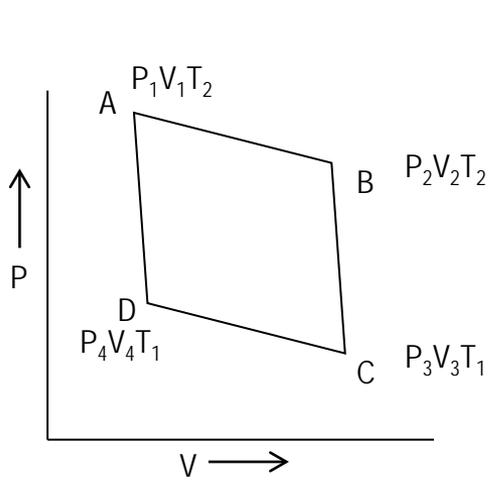At the end of expansion, the system is not capable of doing work.
To do work, it has to be brought back to the original condition by an **adiabatic step.** Thus a **cyclic process** is involved.

For a mathematical analysis, let us assume that the working
substance is an ideal gas and the ideal gas is confined in a
weightless frictionless piston.
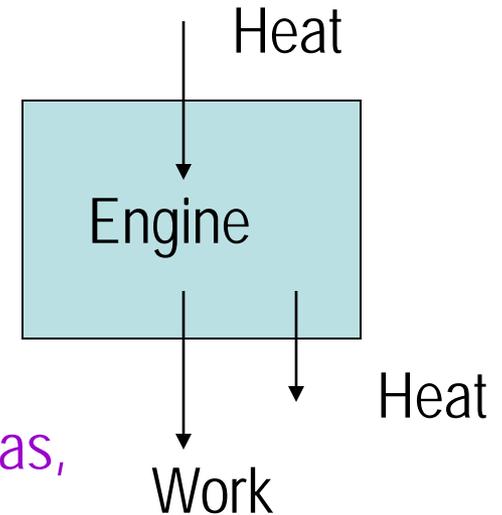
Only mechanical work is analysed!!
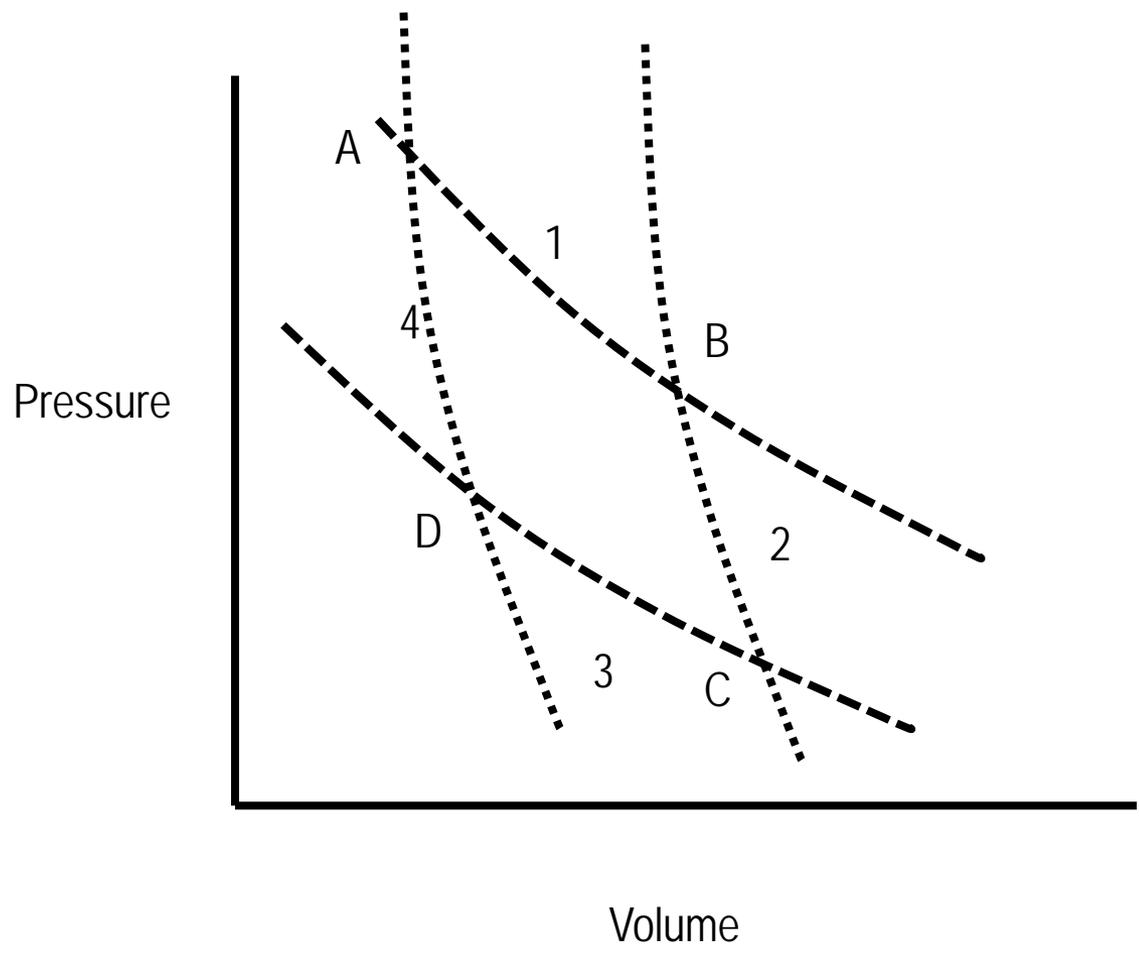
Several ways of looking at the same!

Engine is a cycle!!

It is simple –
Don't you know it is a cyclic process?

$\Delta U = 0$
If we show that $\oint dq_{rev}/T = 0$
we prove that entropy is a state function.

$\Delta U = 0$

$\oint dq_{rev}/T = q_h/T_h + q_c/T_c$

As only two steps have non-zero entropy

$q_h/q_c = -T_h/T_c$

So,

$\oint dq_{rev}/T = 0$

Justification:

$q_h = nRT_h \ln V_B / V_A$ $\qquad q_c = nRT_c \ln V_D/V_C$

$V_A T_h^c = V_D T_c^c$ (1) $c = C_V/R$ $\qquad V_C T_c^c = V_B T_h^c$ (2)

(1) X (2)

$V_A V_C T_h^c T_c^c = V_D V_B T_h^c T_c^c$

$V_A/V_B = V_D/V_C$

$q_c = nRT_c \ln V_D/V_C = nRT_c \ln V_A/V_B = - nRT_c \ln V_B/V_A$

$\dfrac{q_h}{q_c} = \dfrac{nRT_h \ln(V_B/V_A)}{-nRT_c \ln(V_B/V_A)} = \dfrac{-T_h}{T_c}$

Is it valid for all gases?
The efficiency of an engine is, ε = Work done/ Heat absorbed = W/q
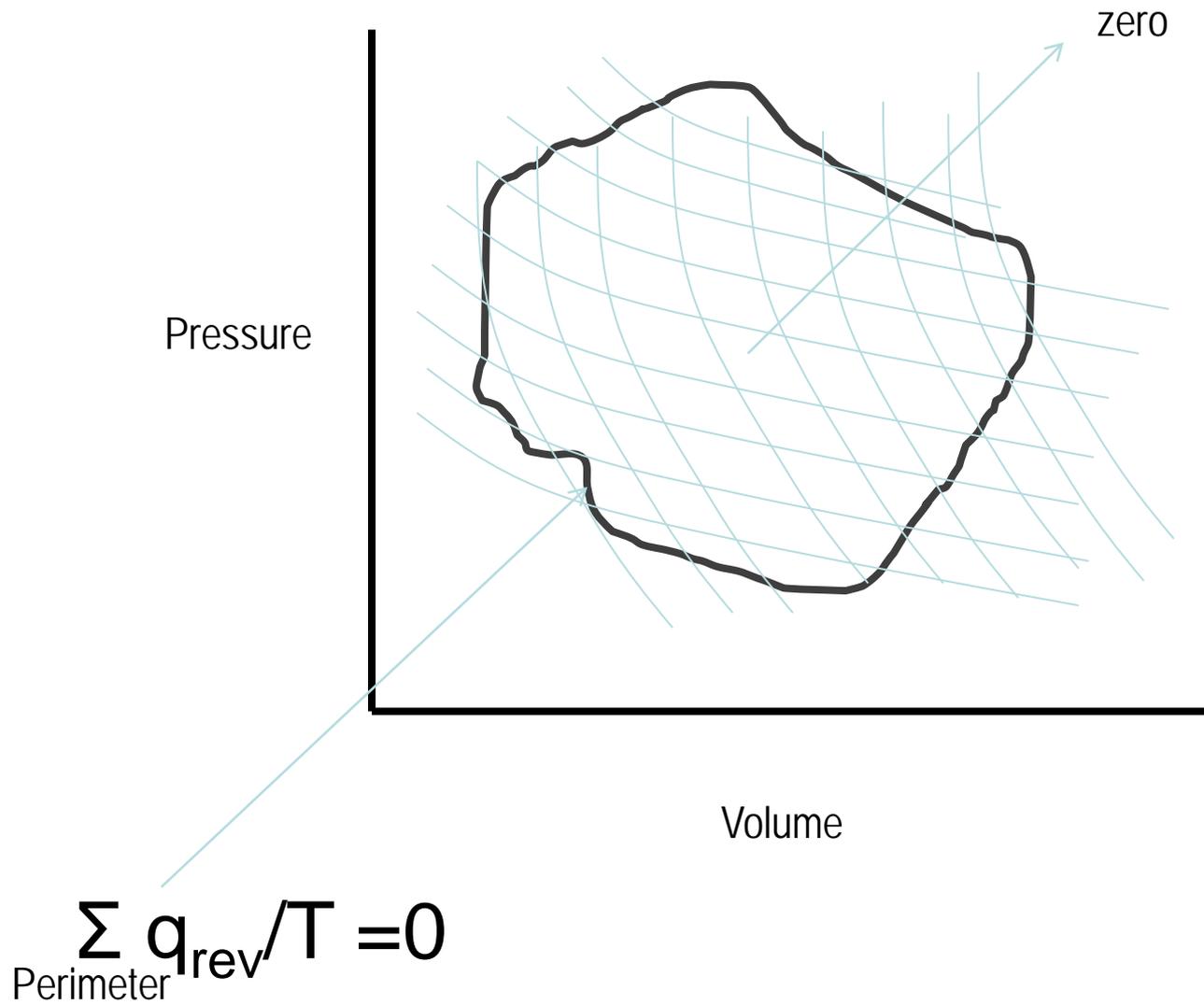
$W = q_h + q_c$

Efficiency, $\varepsilon = W/q_h = (q_h + q_c)/q_h = 1 + q_c/q_h = 1 - T_c/T_h$

Remember that $q_c < 0$

Efficiency is independent of the working fluid. Carnot engine says that for all processes, irrespective of materials, entropy is a state function.

Engine can work in either direction.

zero

Pressure

Volume

$$\sum_{\text{Perimeter}} q_{rev}/T = 0$$

The Carnot cycle gives the maximum work that can be produced from an engine working between two temperatures. The work required in the refrigerator is the minimum work necessary to transfer heat q_c forms the reservoir at T_c to a reservoir at T_h.

An important consequence: The work required to remove heat increases as T_c decreases.

Since $T_h - T_c$ increases as T_c is decreased
So, $[T_h - T_c]/ T_c$ increases fast

If T_c is zero, w would go to infinity.

The value of w would be very high even if T_c is slightly higher than zero
Thus the amount of work required for decreasing the temperature increases as temperature is decreased and it approaches infinitely as absolute zero is achieved.

This fact is expressed as
"unattainability of absolute zero"

Other ways of looking at:

It is interesting to consider the following two special cases:

1. If $T_1 = 0$ efficiency is maximum. Thus the complete conversion of heat to work is possible only if the sink temperature is zero.

2. If $T_2 = T_1$ efficiency is zero that is to say that if the machine works in an isothermal cycle, no work can be produced.

No perpetual motion machine of the first kind is possible.

We saw the change for the system.

What about surroundings?

Surroundings is a reservoir of constant volume (constant pressure)

Heat exchange changes internal energy, which is an exact differential.

So, $dq_{surr} = dU_{surr}$

$$\Delta S_{surr} = dq_{surr}/T_{surr}$$

Regardless of how the transfer is brought about
(reversible or irreversible)

For an adiabatic change, $\Delta S_{surr} = 0$