

Lecture 2

Entropy and Second Law

Etymology: Entropy, entropie in German.

En from energy and trope – turning toward

Turning to energy

System

Surroundings

Characterization of a system

Based on properties

(1) intensive properties and (2) extensive properties

Types of systems

(1) open, (2) closed, and (3) isolated systems.

(1) homogeneous or (2) heterogeneous

Chemical system

Phase, Component

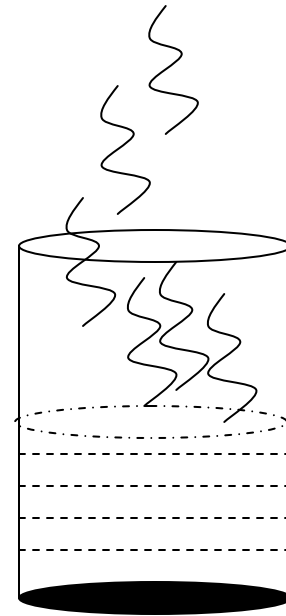
Process, Path

State function, Path function

First Law

$$dU = dq - dw$$

$$w = \int (nRT/V) dV = nRT \ln V_f/V_i$$



Enthalpy, $H = U + PV$

State function

Thermochemistry

Hess's Law

Lavoisier – Laplace Law

Born-Haber Cycle

Kirchhoff's equation

Equipartition principle

Motivation for a “Second Law”

First law allows us to calculate the energy changes

But does not predict the feasibility

The direction of process cannot be predicted by first law

But in natural processes, the direction can be predicted

Is there a parameter to predict spontaneity?

Sadi Carnot

French Physicist: 1796 – 1832

1824 → 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.



Carnot's cycle

How does a system produce work?

The property of natural systems to attain equilibrium has been used to derive work.

Eg. Hydroelectric power stations, steam engines, rockets, etc.

In the operation of a heat engine, heat is converted to work.

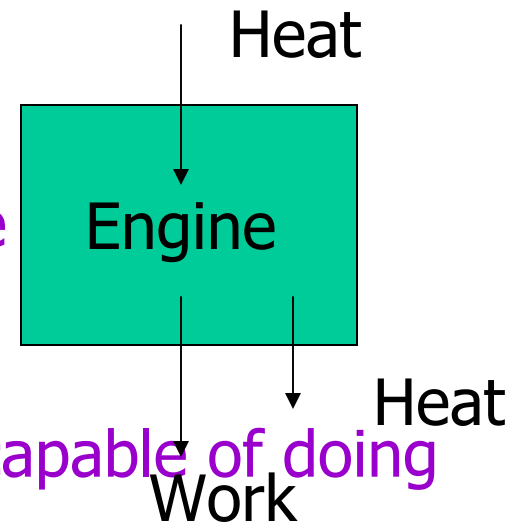
In the process of doing work, heat is absorbed from a hot body and a part of it is transferred to a cold body.

The efficiency of such an engine is,

$$\begin{aligned}\varepsilon &= \text{Work done/ Heat absorbed} \\ &= W/q\end{aligned}$$

Well, how do we analyse efficiency of an engine?

Carnot formulated a method.



1. In the Carnot engine, a heat engine is made to do work between temperatures T_2 and T_1 .

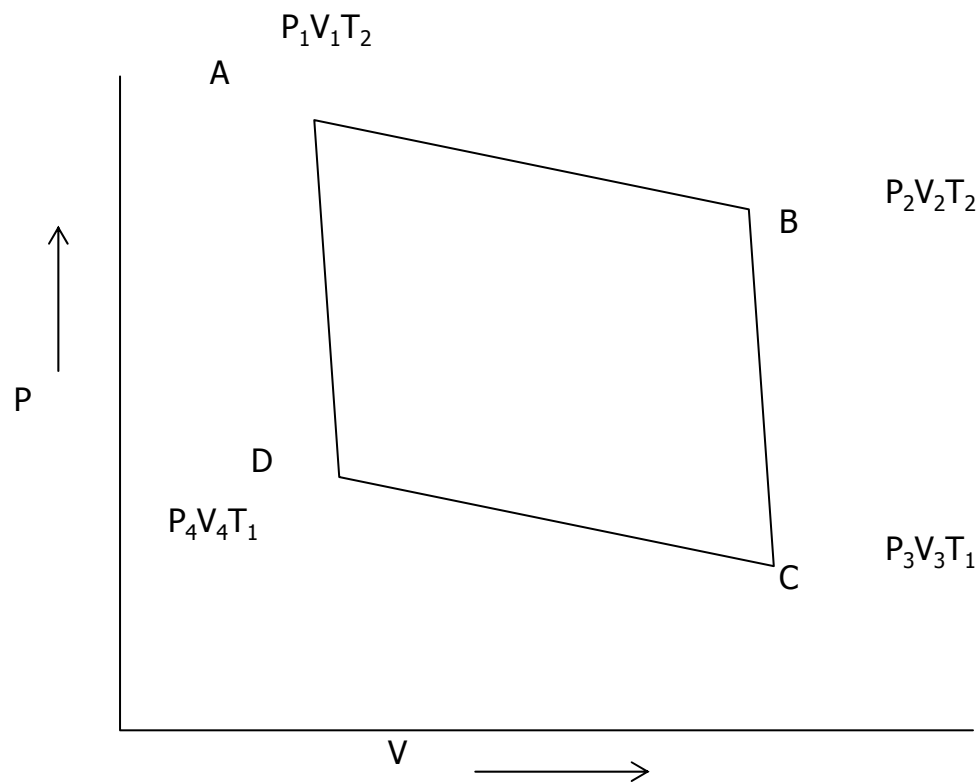
2. At the end of expansion, the system is not capable of doing work.

3. To do work, it has to be brought back to the original condition by an **adiabatic step**. Thus a **cyclic process** is involved.

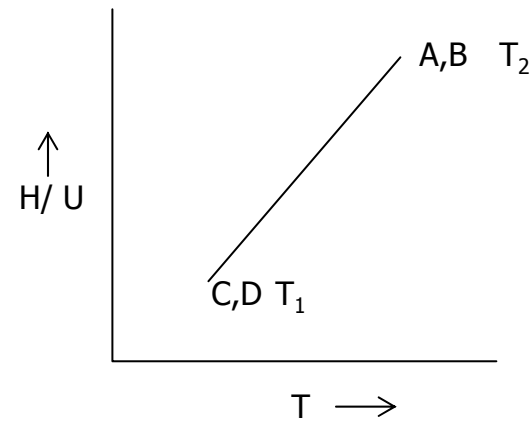
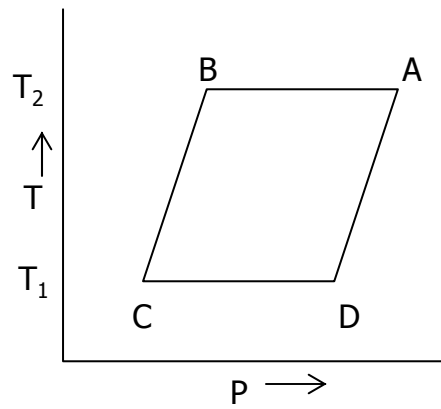
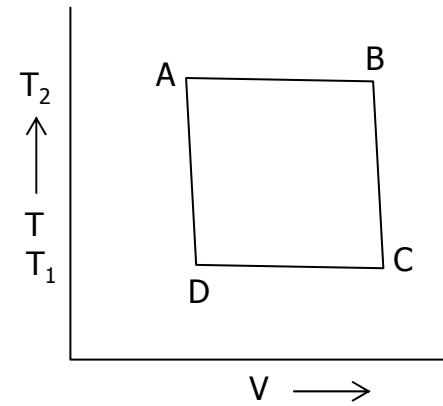
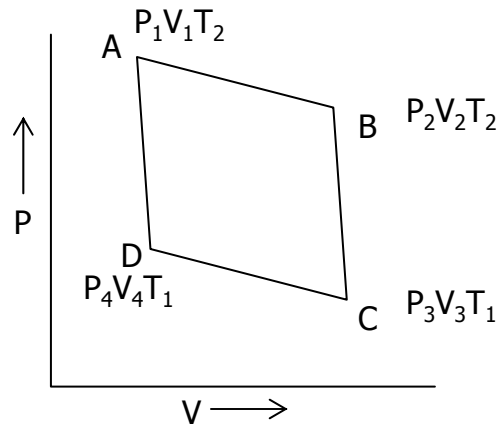
For a mathematical analysis, let us assume that the working substance is an ideal gas and the ideal gas is confined in a weightless frictionless piston.

In an **isothermal reversible expansion** of an ideal gas, $\Delta U = 0$ and $q = W$.

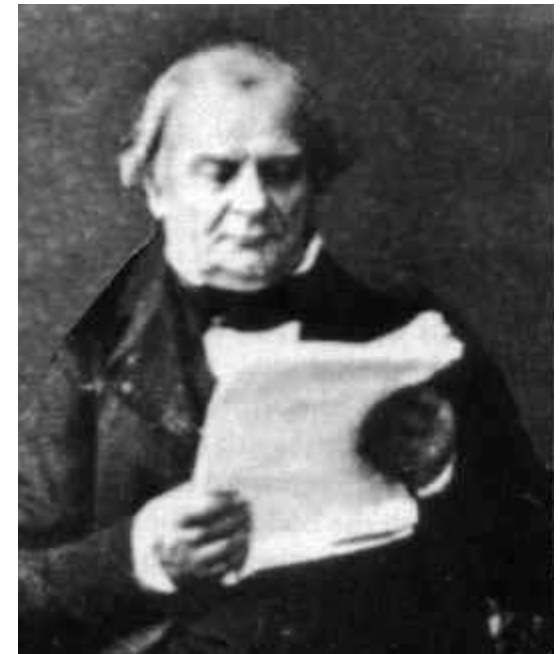
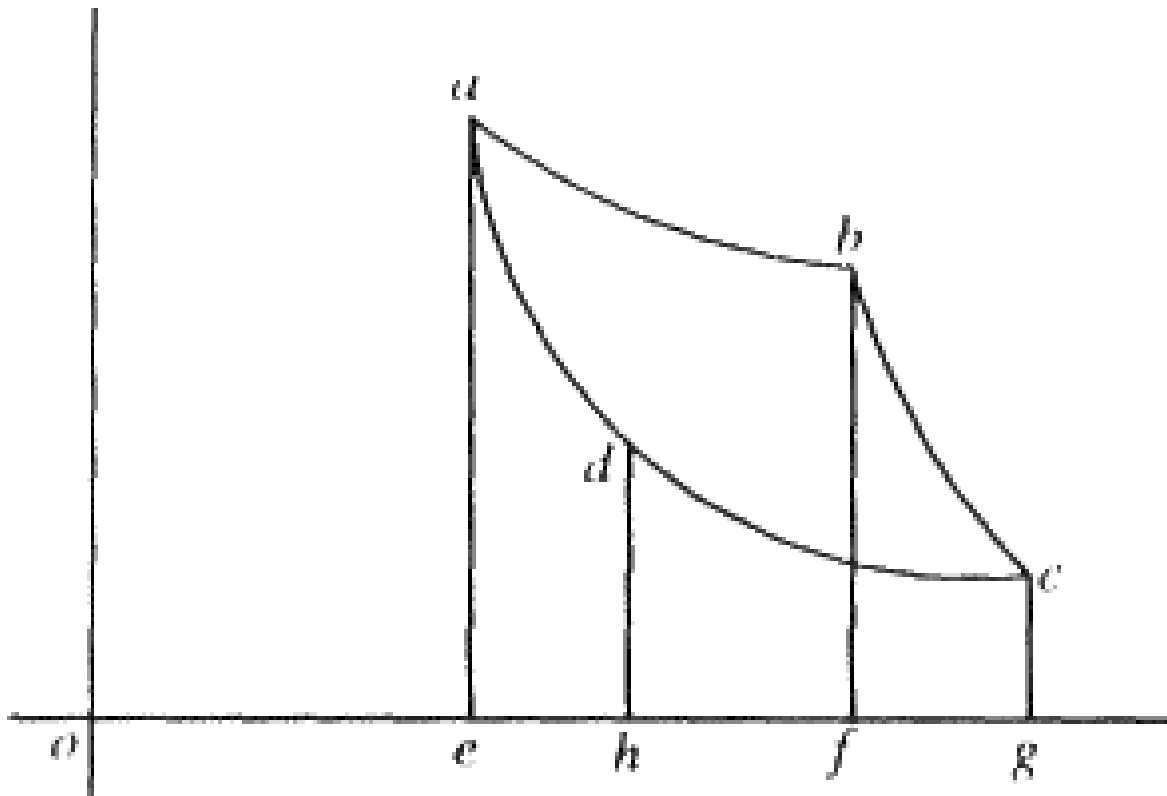
Only mechanical work is analysed!!



What is that cycle?



Several ways of looking at the same!



Benoit Paul Emile Clapeyron

Born: 26 Feb 1799 in Paris, France

Died: 28 Jan 1864 in Paris, France

Engine is a cycle!!

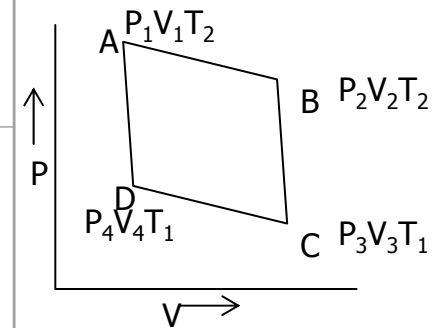
It is simple –
Equation for a cyclic process...

$$\Delta U = 0$$

$$\Delta U = q - W$$

Four steps in the Carnot's engine

N o.	Step	Process	Heat gained	Heat Lost	Work done by gas	Work done on gas
1	A→B	Reversible Isothermal Expansion ($V_2 - V_1$) at T_2	q_h	-	W_1	-
2	B→C	Reversible adiabatic Expansion $V_2 - V_3$	0	0	W_2	-
3	C→D	Reversible isothermal compression ($V_3 - V_4$) at T_1	0	$-q_c$	-	$-W_3$
4	D→A	Reversible adiabatic compression $V_4 - V_1$	0	0	-	$-W_4$



$$\begin{aligned}\Delta U &= \text{Heat absorbed} - \text{Work done} \\ &= (q_h + (-q_c)) - [W_1 + W_2 - W_3 - W_4]\end{aligned}$$

$$\Delta U = q_h - q_c - W$$

$$\text{Where } W = W_1 + W_2 - W_3 - W_4$$

Since $\Delta U = 0$; $W = \text{work done} = \text{heat absorbed}$

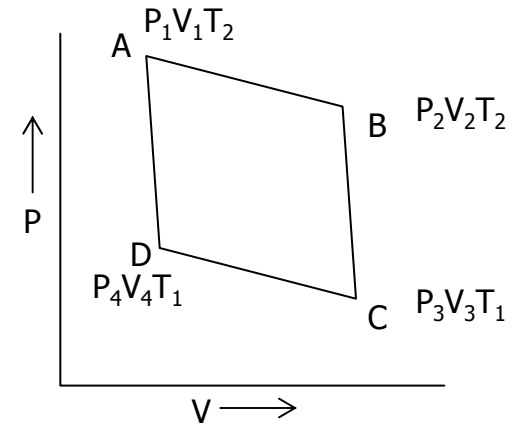
$$W = q_h - q_c$$

$$\text{Efficiency } \varepsilon = W/q_h = (q_h - q_c)/q_h = 1 - q_c/q_h$$

Thus $\varepsilon < 1$

If efficiency has to be 100 %, $q_c = 0$ no heat should return to sink.

Perpetual machine of the second kind.



Carnot engine is reversible

For the reverse cycle, q and w are equal in magnitude but opposite in sign. Reverse engine absorbs q_c from sink and liberates q_h to the source. This engine is called a heat pump or refrigerator. Efficiency of the Carnot's engine is the same whether it works in the forward or reverse direction. Coefficient of performance of the refrigerator,

$$\begin{aligned}\eta &= -w/q_c = (q_h - q_c)/q_c \\ -w &= [(q_h - q_c)/q_c]q_c \\ &= [T_2 - T_1 / T_1] q_c\end{aligned}$$

The second law as defined by Kelvin and Plank is, "it is impossible to construct a machine, operating in cycles, which will produce no effect other than the absorption of heat from a reservoir and its conversion into an equivalent amount of work".

As per the statement of Second Law by Kelvin, "no process is possible by which heat is completely converted to work". Every engine when constructed will absorb heat from a hot body and transfer part of it to the surroundings. There is no way to generate work completely from absorbed heat.

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 from the reservoir at T_1 to a reservoir at T_2 .

An important consequence: The work required to remove heat increases as T_1 decreases.

Since $T_2 - T_1$ increases as T_1 is decreased
So, $[T_2 - T_1]/T_1$ increases fast

If T_1 is zero, w would go to infinity.

The value of w would be very high even if T_1 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"

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.

Baron Kelvin of Largs (William Thomson) Phil. Mag. 4 (1852).

Thermodynamic temperature scale

The efficiency of the Carnot engine depends on the heat transferred not on the working substance.

If θ_1 and θ_2 are the two temperatures, the ratio of the heat absorbed,

$$\begin{aligned}q_2/q_1 &= \theta_2/\theta_1 \\ q_2 - q_1/q_2 &= \theta_2 - \theta_1/\theta_2 = \epsilon\end{aligned}$$

$$\text{If } \theta_1 = 0, \epsilon = 1$$

The thermodynamics scale of temperature is related to absolute scale.

$$W = W_1 + W_2 + W_3 + W_4$$

$$W = RT_2 \ln V_2/V_1 + C_v (T_2 - T_1) + RT_1 \ln V_4/V_3 - C_v (T_2 - T_1)$$

$$W_1 = RT_2 \ln V_2/V_1; W_2 = -C_v (T_1 - T_2); W_3 = RT_1 \ln V_4/V_3; W_4 = -C_v (T_2 - T_1)$$

$$W = RT_2 \ln V_2/V_1 - RT_1 \ln V_3/V_4$$

$$[T_2/T_1 = (V_3/V_2)^{\gamma-1} = (V_4/V_1)^{\gamma-1}] = [V_3/V_2 = V_4/V_1 \text{ or } V_3/V_4 = V_2/V_1]$$

$$W = RT_2 \ln V_2/V_1 - RT_1 \ln V_2/V_1$$

$$= R \ln V_2/V_1 (T_2 - T_1)$$

$$\epsilon = W/q = R ((T_2 - T_1) \ln V_2/V_1) / (RT_2 \ln V_2/V_1) = [T_2 - T_1]/T_2$$

$$\epsilon = [(\theta_2 - \theta_1) / \theta_2] = (T_2 - T_1)/T_2$$

Thus absolute temperature scale is the same as thermodynamics temperature scale.

Efficiency depends only on the temperatures, not on the working substance.

Lower the temperature of the sink for a given source temperature, higher will be the efficiency. However, it is not convenient to keep the sink temperature lower than the atmospheric temperature.

Therefore, the source temperature has to be high for maximum efficiency.

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.

Entropy

For Carnot engine,

$$\epsilon = (T_2 - T_1)/T_2 = (q_2 - q_1)/q_2$$

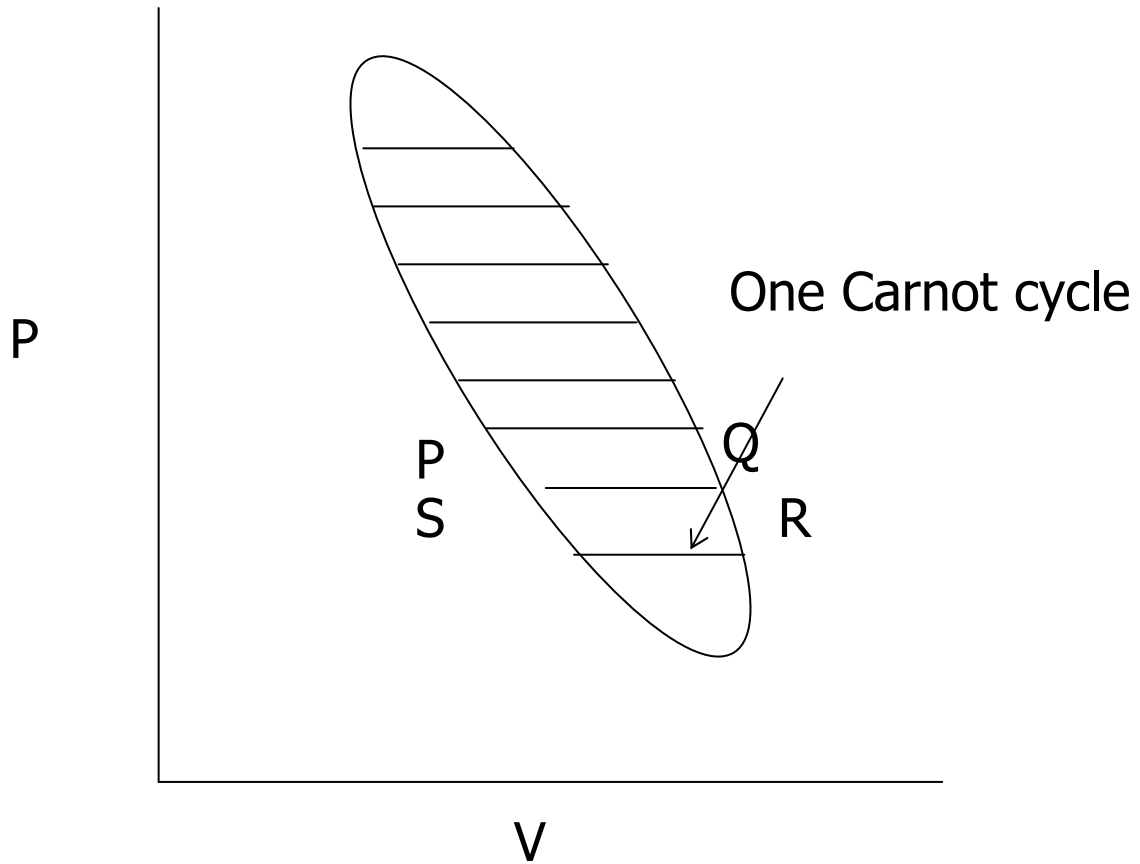
$$q_1/q_2 = T_1/T_2$$

$$q_2/T_2 - q_1/T_1 = 0$$

$$q_2/T_2 + (-q_1)/T_1 = 0$$

$$\Sigma q_{\text{rev}}/T = 0$$

It can be shown that $q_{\text{rev}}/T = 0$ for any cyclic reversible process



In the limit of infinitesimal cycles, $\sum q_{rev}/T = 0$, for any cycle

What did Carnot cycle say?

dq/T is a state function

That is dS !!

$dq/T = dS$ or $dq = TdS$

No, not for all dq , but for dq_{rev}

What did Carnot cycle tell us really?

It said that entropy is a state function.

The fact that for a cyclic process, $dq/T = 0$

How is this?

For a cyclic process, $\Delta U = 0$

$$= q - w$$

$$q_{\text{rev}} = w_{\text{rev}}$$

$$\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = q_{\text{rev}}/T = nR \ln V_f/V_i$$

This is for a perfect gas undergoing an expansion

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.

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

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

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

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