Lecture 6
Entropy and Second Law

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

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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".

Spontaneous process has to transfer part of the energy.

Processes moving from non-equilibrium to equilibrium states are called spontaneous.

Energy minimum leads to spontaneity?
Examples: Expansion into vacuum
Energy change of surroundings
Both these do not reduce energy.

Partitioning of energy could be the reason for spontaneity.
Partitioning implies molecular basis of energy.

Entropy

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

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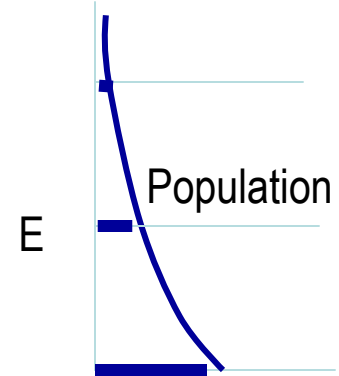
$\Delta S = q_{rev}/T = 1/T \int_i^f dq_{rev} = nR\ln V_f/V_i$

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

Adiabatic, ΔS_{sur} = 0

Statistical meaning of entropy

Population

E

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, Ni found in a given state with energy E_i, when the system is at thermal equilibrium at T is,

$$S = k \ln W$$

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

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

Entropy as a state function

Carnot's cycle or **Carnot** **cycle shows that.**

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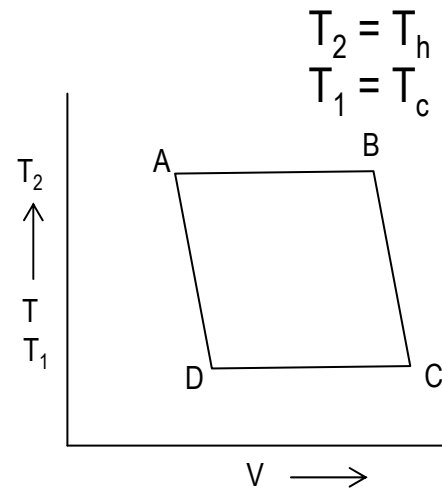To do work, it has to be brought back to the original condition by an **adiabatic step.** Thus a **cyclic process** is involved.

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.
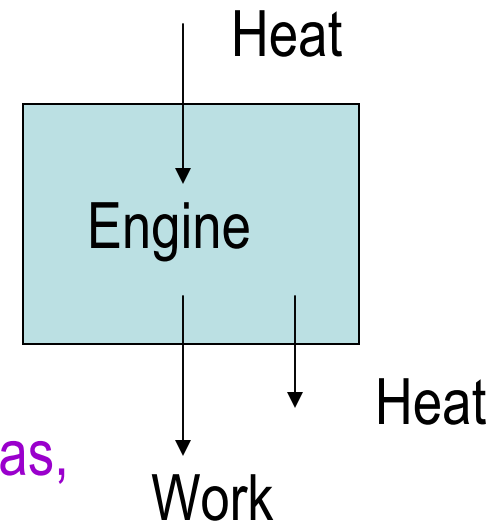
Only mechanical work is analysed!!

Pressure

Volume

$T_2 = T_h$
$T_1 = T_c$
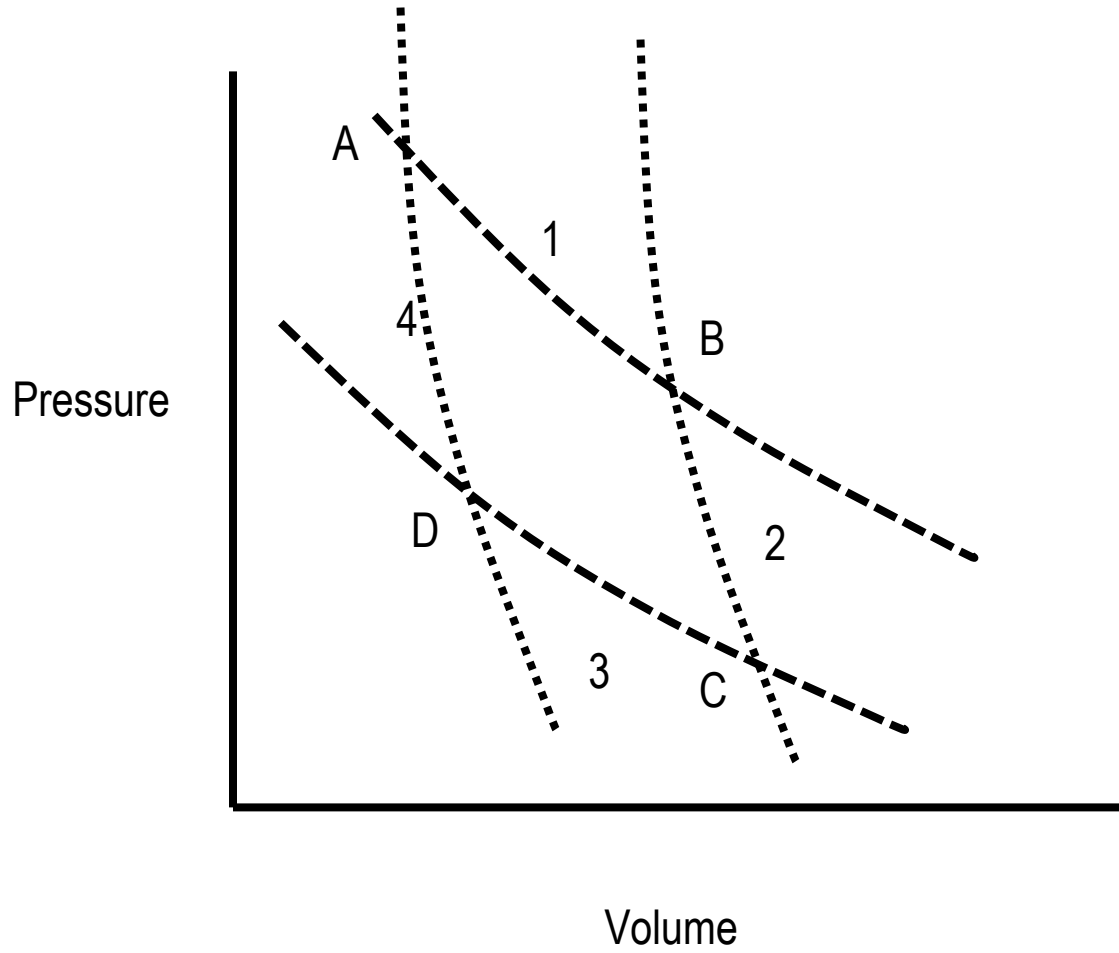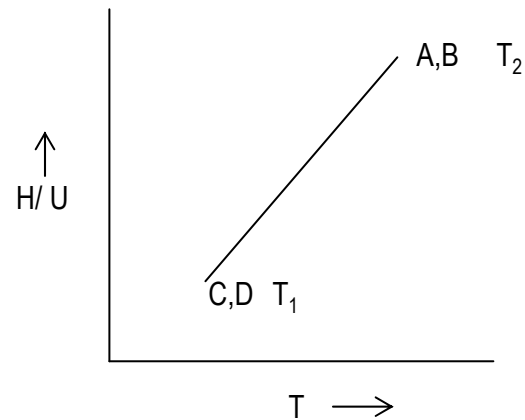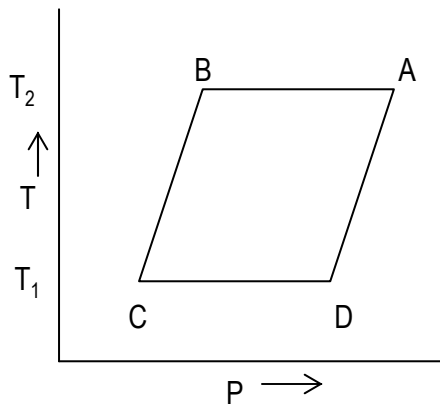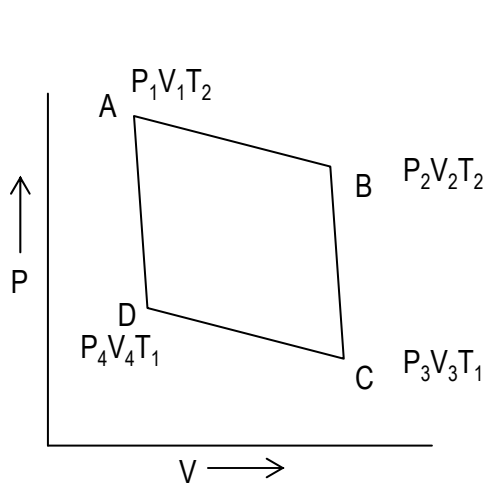
Several ways of looking at the same!

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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 $\quad = q_h + q_c$

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.

zero

Pressure

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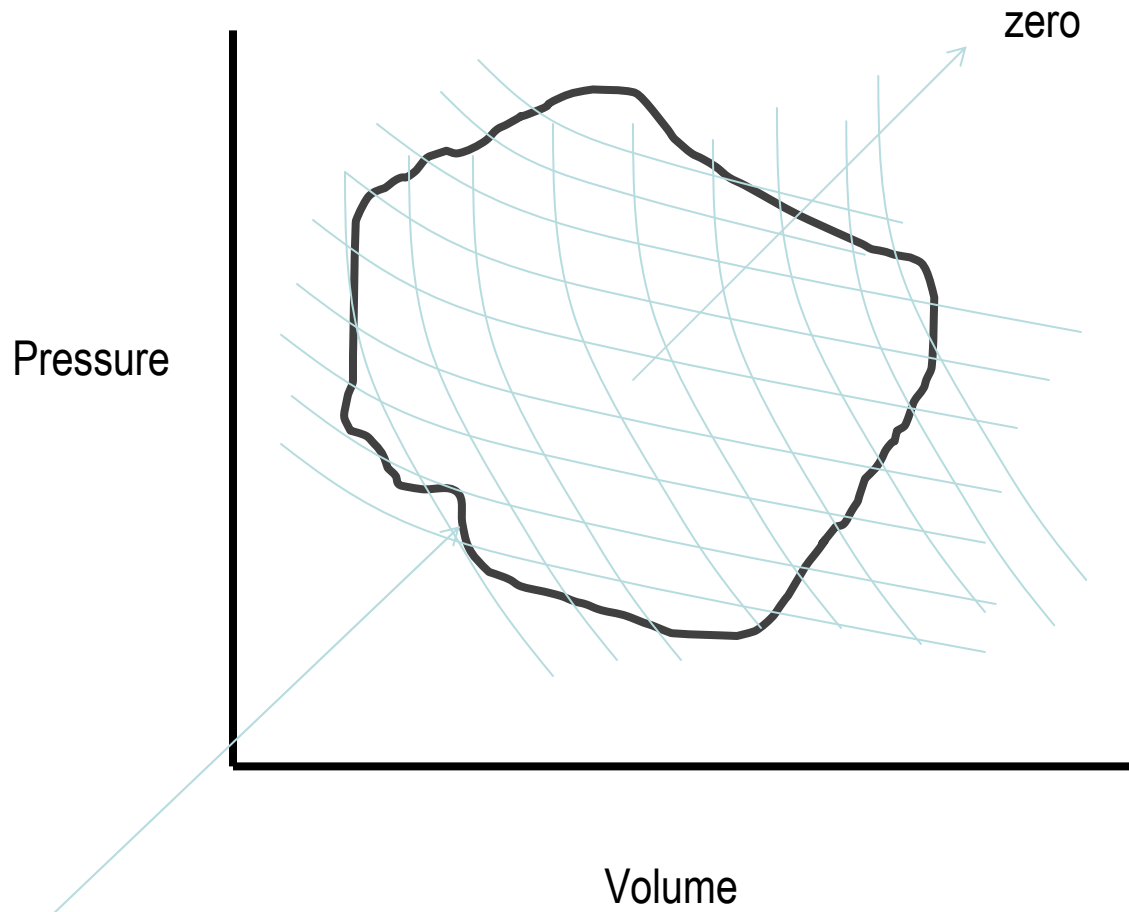
$$\sum_{\text{Perimeter}} q_{rev}/T = 0$$

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,

$$c = \text{energy transferred/work required} = q_c/W$$

More work required, lower is the coefficient of performance

$$1/c = (q_h - q_c)/q_c$$

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". It can also be stated as suggested by Clausius, "it is impossible to construct a machine operating in cycles to transfer heat from a colder body to a hotter body without any other effect".

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.

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).**

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_1 to a reservoir at T_2.

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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"

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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,

$$q_2/q_1 = \theta_2 / \theta_1$$

$$q_2 - q_1/q_2 = \theta_2 - \theta_1 / \theta_2 = \in$$

If $\theta_1 = 0$, $\in = 1$

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The thermodynamics scale of temperature is related to absolute scale.

$W = W_1 + W_2 + W_3 + W_4$

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

$W1 = RT_2 \ln V_2/V_1; W_2 = - C_v (T_1 - T_2); W_3 = RT_1 \ln V_4/V_3; W_4 = -C_v (T_2 - T_1)$

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

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

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

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

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

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

Thus absolute temperature scale is the same as thermodynamic 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.

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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.

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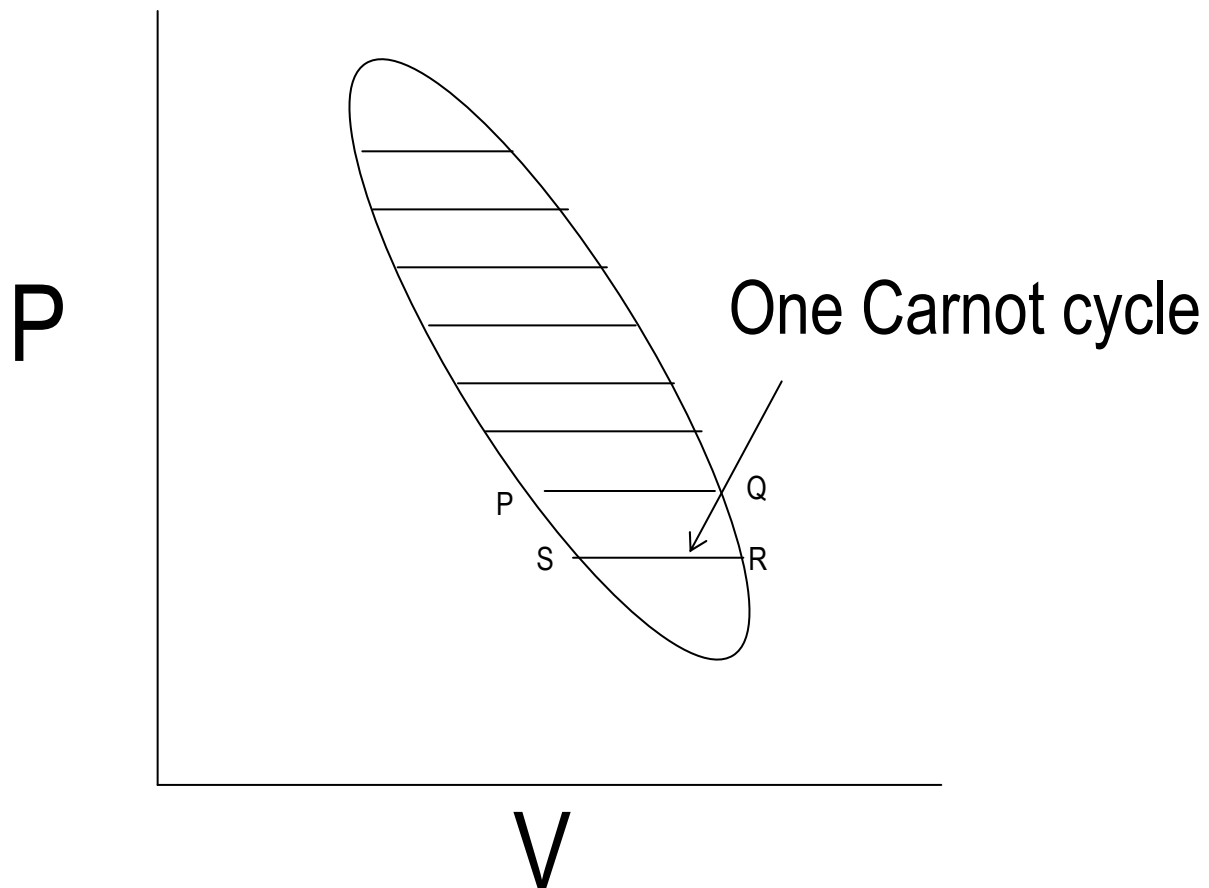
Entropy

For Carnot engine,

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

$q_1/q_2 = T_1/T_2$

$q_2/T_2 - q_1/T_1 = 0$

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

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

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

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P

V

One Carnot cycle

P Q
S R

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

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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}

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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
$q_{rev} = w_{rev}$

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

This is for a perfect gas undergoing an expansion

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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, $\Delta S_{surr} = 0$

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