3 Introduction to the Second Law of Thermodynamics

The First Law introduces a state function, the internal energy ***U***. the First Law permits us to assess *What changes are permissible? only those changes may occur for which the internal energy of an isolated system remains constant.*

The Second Law introduces a state function, entropy ***S***. The Second Law permits us to identify the spontaneous changes among those permissible changes. *Is one state of the system accessible from another state of the system by a* <u>*spontaneous*</u> *change?*

To prepare a foundation for the mathematical definition of entropy we consider characteristics of cyclic transformations, in particular the Carnot cycle.

3.1 The Carnot Cycle

Sadi Carnot investigated the principles governing the transformation of thermal energy heat into mechanical energy, work. He based his discussion on a cycle of 4 <u>*reversible*</u> steps:

step 1. Isothermal expansion
step 2. Adiabatic expansion
step 3. Isothermal compression
step 4. Adiabatic compression

The material composing the system is confined in a cylinder fitted with a piston. The cycle uses *two heat reservoirs*, one reservoir at a higher temperature T_h and the other reservoir at a lower temperature T_c.

heat reservoir — a system which has the same temperature everywhere within it, this temperature is unaffected by the transfer of any desired quantity of heat into or out of the reservoir.

The mass of the system is fixed; the state can be described by any two of p, V, or T. The original state: The cylinder is immersed in a heat reservoir at temperature T_h, under which conditions the material has volume V_A and pressure p_A.

step 1. Isothermal expansion

In this step, the system is expanded isothermally from the initial volume V_A to a volume V_B.

The cylinder is now taken out of the reservoir, insulated, and then,

step 2. Adiabatic expansion

The system is expanded adiabatically from V_B to V_C. In this step the temperature of the system drops from T_h to a lower temperature T_c.

The insulation is removed and the cylinder placed in a heat reservoir at T_c. and then,

step 3. Isothermal compression

The system is compressed isothermally (at T_c) from V_C to V_D.

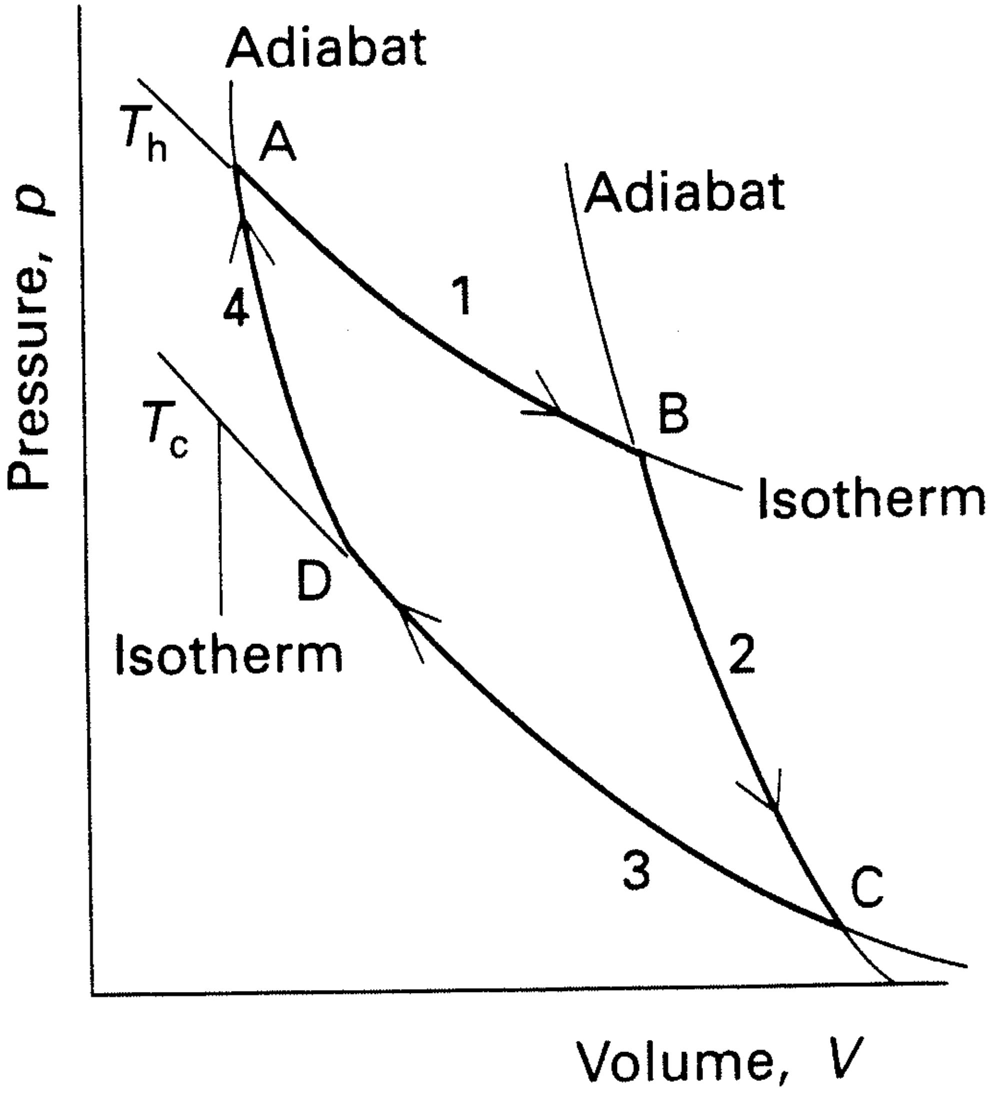
The cylinder is removed from the reservoir and insulated again, and then,

step 4. Adiabatic compression

The system is compressed adiabatically from V_D to V_A, the original volume. In this adiabatic compression, the temperature rises from T_c to T_h, the original temperature.

Thus, the system is restored to its initial state.

step	initial state	final state	First Law statement
1	T_h, p_A, V_A	T_h, p_B, V_B	$\Delta \boldsymbol{U} = q_h + W_1$
2	T_h, p_B, V_B	T_c, p_C, V_C	$\Delta \boldsymbol{U} = W_2$
3	T_c, p_C, V_C	T_c, p_D, V_D	$\Delta \boldsymbol{U} = q_c + W_3$
4	T_c, p_D, V_D	T_h, p_A, V_A	$\Delta \boldsymbol{U} = W_4$
cy			$\Delta \boldsymbol{U}_{cy} = 0$



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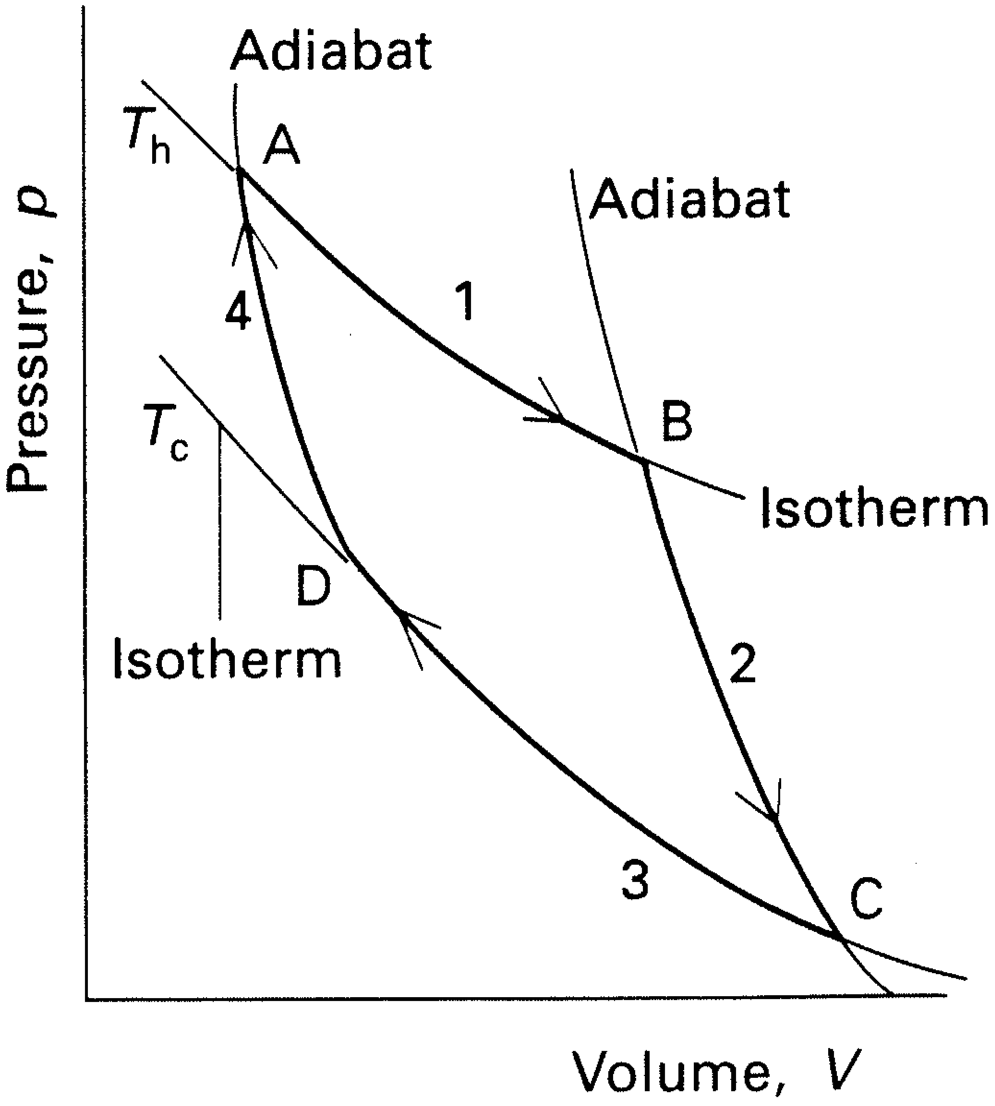
1	$T_h,\ p_A, V_A$	$T_h,\ p_B, V_B$	$\Delta \boldsymbol{U} = q_h + W_1$
2	$T_h,\ p_B, V_B$	$T_c,\ p_C, V_C$	$\Delta \boldsymbol{U} = W_2$
3	$T_c,\ p_C, V_C$	$T_c,\ p_D, V_D$	$\Delta \boldsymbol{U} = q_c + W_3$
4	$T_c,\ p_D, V_D$	$T_h,\ p_A, V_A$	$\Delta \boldsymbol{U} = W_4$
cy			$\Delta \boldsymbol{U}_{cy} = 0$



$W_{cy} = W_1 + W_2 + W_3 + W_4$

$q_{cy} = q_h + q_c$

$\Delta \boldsymbol{U}_{cy} = 0 = W_{cy} + q_{cy} \qquad -W_{cy} = q_h + q_c$

If W_{cy} is negative (work has flowed from the system across the boundary and appeared in the surroundings), any work produced by the system has been produced at the expense of the thermal energy of the surroundings. that is, heat ($q_h + q_c$) has flowed from the surroundings to the system at the same time.

It is possible to devise a cycle so that work appears in the surroundings. It can be done in ways using reservoirs at many different temperatures, or it can be done using only 2 reservoirs at different temperatures, as in the Carnot cycle. Experience has shown that (Kelvin's statement of the Second Law:) *it is impossible for a system operating in a cycle and connected to a single heat reservoir to produce a positive amount of work in the surroundings.*

Experience shows that if a heat engine operates between two temperature reservoirs so that a positive amount of work appears in the surroundings, i.e., $-W_{cy} > 0$*, then* q_h *the heat withdrawn from the high temperature reservoir is positive (heat flows from the high temperature reservoir to the system) and* q_c *the heat withdrawn from the low temperature reservoir is negative (heat flows from the system to the low temperature reservoir) .*

efficiency of a heat engine — ratio of the work produced in the surroundings to the quantity of heat extracted from the high-temperature reservoir.

$$\varepsilon = -W_{cy} / q_h$$

For the Carnot cycle, $-W_{cy} = q_h + q_c$
so that $\varepsilon = (q_h + q_c) / q_h = 1 + (q_c / q_h) < 1$
The efficiency is the fraction of the heat withdrawn from the high-temperature reservoir which is converted into work in the cyclic process.

Consider the efficiencies of two engines operating in a cycle between the same two heat reservoirs. *Is it possible that the efficiencies of these two engines are different?*

Let two engines E_r and E' both operate in a cycle between the same two heat reservoirs. The engines may be designed differently and may use different working substances. Let E_r be a reversible engine and E' any engine at all, reversible or not.

For engine E_r, *reversible*, therefore

$-W_{cy} = q_h + q_c$ forward cycle

$-(-W_{cy}) = -(q_h + q_c)$ reverse cycle

For the engine E'

$-W_{cy}' = q_h' + q_c'$ forward cycle

Suppose we run engine E_r in its reverse cycle and couple it to engine E' running in the forward cycle. For this composite engine,

$W_{cy} + -W_{cy}' = -(q_h + q_c) + q_h' + q_c'$

just by summing the individual effects of the appropriate cycles. Let us adjust E_r so that the composite engine produces no work in the surroundings, i.e., adjust E_r until

$W_{cy} \ -W_{cy}' = 0$.

Then, $0 = -(q_h + q_c) + q_h' + q_c'$

or $(q_h - q_h') = -(q_c - q_c')$

What if the efficiency of E′ is greater than E_r?

Then, $\varepsilon' = (W_{cy}')/q_h' \quad > \quad \varepsilon = (W_{cy})/q_h$

Then, $1/q_h' \ > \ 1/q_h \quad$ or $q_h > q_h'$

In summary

	E_r reverse	E′ forward	composite engine
Work produced	W_{cy}	$-W_{cy}'$	0
Heat out of T_h	$-q_h$	q_h'	$q_h' - q_h = -$
Heat out of T_c	$-q_c$	q_c'	$q_c' - q_c = +$
First law	$W_{cy} - q_h - q_c = 0$	$-W_{cy}' + q_h' + q_c' = 0$	$0 = (q_h' - q_h) + (q_c' - q_c)$

Note what we have here, the system has a negative heat ($q_h' - q_h$), that is, the composite engine puts a positive quantity of heat into the reservoir at T_h and extracts an equal quantity of heat from the reservoir at T_c. What a gadget! We could imagine the cold end to be the inside of an icebox and the hot end to be the inside of an oven. Our engine will neither create nor use work, but manage to pump heat from the cold end to the hot end, all without benefit of Commonwealth Edison. This is impossible to build (*perpetual motion machine of the second kind*).

The argument which led to this impossible engine was based only on the First Law and the assumption that the efficiency of E′ is greater than E_r! Therefore, <u>the efficiency of any engine must be less than or equal to the efficiency of a reversible engine</u>, both operating between the same two temperatures. $\varepsilon' \leq \varepsilon$

Now consider two *reversible* engines with efficiencies ε' and ε''. since the second one is reversible, the efficiency of the first must be less than or equal to the second. $\varepsilon' \leq \varepsilon''$. But the first is reversible so $\varepsilon'' \leq \varepsilon'$ also.

Thus, $\varepsilon' = \varepsilon''$ must be true.

All reversible engines operating between the same two temperature reservoirs have the same efficiency.

The equality dictates that the efficiency of a reversible engine does not depend on the working substances in the engine, only the temperatures of the reservoirs. Hence *the efficiency of reversible engines is a function only of the temperatures of the reservoirs.*

$\varepsilon = f(T_h , T_c)$. Since any substance used in the reversible engine gives the same efficiency, make it an ideal gas for easy calculations.

step	general case	ideal gas
1	$\Delta \boldsymbol{U} = q_h + W_1$	$0 = q_h - RT_h\ln(V_B/V_A)$
2	$\Delta \boldsymbol{U} = W_2$	$\int C_V \mathrm{d}T = W_2$ $C_V \mathrm{d}T/T = -R\mathrm{d}V/V$ $C_V \ln(T_c/T_h) =$ $-R\ln(V_C/V_B)$
3	$\Delta \boldsymbol{U} = q_c + W_3$	$0 = q_c - RT_c\ln(V_D/V_C)$
4	$\Delta \boldsymbol{U} = W_4$	$\int C_V \mathrm{d}T = W_4$ $C_V \mathrm{d}T/T = -R\mathrm{d}V/V$ $C_V \ln(T_h/T_c) =$ $-R\ln(V_A/V_D)$ $W_4 =$
cycle	$W_{cy} =$ $W_1 + W_2 + W_3 + W_4$	$W_{cy} = - RT_h\ln(V_B/V_A)$ $+\int^{Tc}_{Th} C_V \mathrm{d}T$ $-RT_c\ln(V_D/V_C)$ $+\int^{Th}_{Tc} C_V \mathrm{d}T$ $= - R(T_h - T_c)\ln(V_B/V_A)$

from steps 2 and 4: $\ln(V_C/V_B) = -\ln(V_A/V_D)$ or $V_B/V_A = V_C/V_D$

$W_{cy} = -R(T_h - T_c)\ln(V_B/V_A)$ depends on the temperatures of the two reservoirs and on the ratio (V_B/V_A) (the compression ratio) for an ideal gas as the working substance in a reversible cycle.

$$\text{Efficiency, } \varepsilon \equiv -W_{cy}/q_h$$
$$= (q_h + q_c)/q_h$$

for any engine based on **2 temperature reservoirs**

$$= \frac{R(T_h - T_c)\ln(V_B/V_A)}{RT_h \ln(V_B/V_A)}$$
$$= (T_h - T_c)/T_h = 1 - (T_c/T_h)$$

for any ***reversible*** cycle

For reversible cycle

$$\varepsilon = (q_{h,rev} + q_{c,rev})/q_{h,rev}$$
$$= 1 + (q_{c,rev}/q_{h,rev}) = 1 - (T_c/T_h)$$

Therefore,

$$(q_{c,rev}/q_{h,rev}) + (T_c/T_h) = 0, \text{ or}$$
$$(q_{c,rev}/T_c) + (q_{h,rev}/T_h) = 0$$

Here is something which when summed up for the cycle is zero, i.e., a state function!

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

3.2 The Thermodynamic Definition of Entropy

We have actually shown this only for reversible cycles that involve only 2 temperatures, but can generalize the proof to any cycle whatsoever by constructing appropriate combinations of Carnot cycles.

Define $\mathrm{d}\boldsymbol{S} \equiv \text{đ}q_{rev}/T$ an exact differential

3.3 The Clausius Inequality

For <u>irreversible</u> cycles,

$$\varepsilon' = [1 + (q_c / q_h)] \quad < \quad [1 + (q_{c,rev} / q_{h,rev})].$$

By constructing composite cycles with irreversible cycles and running in reverse some of them, it can be shown that:

For other (not reversible) cycles

$$\oint \eth q_{irrev} / T \quad < 0$$

For any change in state,

$$\int \eth q_{irrev} / T \quad < \quad \int \eth q_{rev} / T = \Delta \boldsymbol{S}$$

or $\Delta \boldsymbol{S} \geq \int \eth q_{irrev} / T$ *Clausius inequality*

The Clausius inequality can be applied directly to changes in an isolated system. For any change in state in an isolated system, $\eth q_{irrev} = 0$ since no heat goes in or out of the system. The inequality then becomes

$$\mathrm{d}\boldsymbol{S}_{\text{isolated system}} > 0$$

That is, the requirement for a real transformation in an isolated system is that d***S*** be positive, the entropy must increase.

Any natural change occurring within an isolated system is attended by an increase in entropy of the system. The entropy of an isolated system continues to increase so long as changes occur within it. When the changes cease, the isolated system is in equilibrium and entropy has reached a *maximum* value. Therefore, *the condition of equilibrium in an isolated system is that the entropy have a maximum value*.

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The First Law: $d\boldsymbol{U} = \eth q + \eth W$

If only pressure-volume work is done, then in a *reversible* transformation ($p_{op} = p_{gas}$), $d\boldsymbol{U} = \eth q_{rev} - p\,dV$

Divide by T:

$$\frac{d\boldsymbol{U}}{T} = \frac{\eth q_{rev}}{T} - \frac{p}{T}\,dV$$

using the definition of $d\boldsymbol{S}$

$$\frac{d\boldsymbol{U}}{T} = d\boldsymbol{S} - \frac{p}{T}\,dV$$

$$\boxed{\begin{array}{l} d\boldsymbol{S} = \dfrac{dU}{T} + \dfrac{p}{T}\,dV \qquad\qquad \textit{general} \\ \textit{or} \\ d\boldsymbol{U} = Td\boldsymbol{S} - pdV \end{array}}$$