Is the 2nd law of thermodynamics just a consequence of the 1st law for an ideal gas ?

The question arises from the following reasoning, which apparently brings from A (1st law) to B (2nd law).
Let us postulate the following hypothesis:
− 1st law :   **ΔU = Q – W** , $dU = \delta Q - \delta W$ **(1),**
U being a **state function** (independent on the past history)
(assumed that heat is positive when received by a system, work is positive when done by the system on the outside)
− reversible transformations
(any state during a transformation is an equilibrium state, all heat and work exchanges are reversed if the transformation is accomplished backwards along the same path)
− only ideal gases involved, i.e. $pV = nRT$ (2)   applies and specific heats

$$c_V = \frac{1}{n}\left[\frac{\delta Q}{dT}\right]_V \; ; \; c_p = \frac{1}{n}\left[\frac{\delta Q}{dT}\right]_p \quad (3) \quad \text{are constant}$$

and see what chain of reasoning may be developed.

1. Mayer's relation

$$c_p - c_V = R \qquad (4) \; ,$$

proved as follows.

Let us consider two states 1 and 2 of an ideal gas, represented by the two points (p_1, V_1) and (p_2, V_2) in Clapeyron's plane. Being U a state variable, its variation when passing from state 1 to state 2 will be independent on the transformation path; therefore, with reference to the figure next,

$\Delta U_{132} = \Delta U_{142} = \Delta U_{12}$, paths 1 → 3 → 2 and 1 → 4 → 2 consisting both only of isobaric and isochoric transformations.
Based on 1st law :

$$\Delta U_{132} = Q_{132} - W_{132} = nC_p(T_3 - T_1) + nC_V(T_2 - T_3) - p_1\Delta V \qquad (5')$$
$$\Delta U_{142} = Q_{142} - W_{142} = nC_v(T_4 - T_1) + nC_p(T_2 - T_4) - p_2\Delta V \qquad (5'').$$

For an ideal gas nT = pV/R, by which we can eliminate the temperatures in the (5) and rewrite them completely in terms of pressures and volumes, i.e.
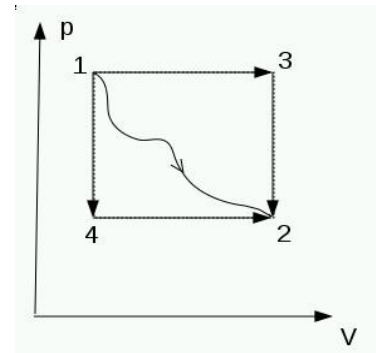
$$\Delta U_{132} = \left(\frac{c_p}{R} - 1\right)p_1\Delta V + \frac{c_V}{R}V_2\Delta p \quad (6') \; ; \quad \Delta U_{142} = \left(\frac{c_p}{R} - 1\right)p_2\Delta V + \frac{c_V}{R}V_1\Delta p \quad (6'')$$

wherein $\Delta V = V_2 - V_1 \; ; \; \Delta p = p_2 - p_1$. Now, by equating $\Delta U_{132} = \Delta U_{142}$ we finally come to the relation:

$$\frac{c_V}{R}\Delta p \Delta V = \left(\frac{c_p}{R} - 1\right)\Delta p \Delta V \quad (7),$$ which must be valid for any transformation starting form point 1 and

ending in point 2, and therefore for transformations for which we may consider $\Delta p \neq 0 \; ; \; \Delta V \neq 0 \; ;$

therefore it must be $\frac{c_V}{R} = \frac{c_p}{R} - 1$, from which Mayer's relation follows: $c_V = c_p - R$.

2. Internal energy and temperature

In an ideal gas the internal energy U depends only on the temperature.

Proof is that by combining Mayer's relation and the equation of ideal gases with e.g. the (6') we obtain:

$$\Delta U_{12}=\Delta U_{132}=\left(\frac{c_p}{R}-1\right)p_1\Delta V+\frac{c_V}{R}V_2\Delta p=\frac{c_V}{R}(p_1\Delta V+V_2\Delta p)=\frac{c_V}{R}nR\Delta T \Rightarrow \Delta U_{12}=nc_V\Delta T$$

(8)

3. Work in an isothermic process

Such work may be found by integrating the ideal gas equation

$$p=\frac{nRT}{V} \Rightarrow W=\int_{V_1}^{V_2} p\,dV=nRT\ln\frac{V_2}{V_1} \quad (9)$$

and is equal to the heat exchange Q, since along an isotherm it must be ΔU=0 (point 2. above, relation (8)).

3. Adiabatic slope

In a *reversible cycle undergone by an ideal gas* , based on 1st law:

$$\delta Q=dW+\delta U=p\,dV+nc_V\,dT=p\,dV+c_V d(\frac{pV}{R}) \text{ ; hence } \delta Q=\frac{1}{R}(c_p p\,dV+c_V V\,dp) \quad (10)$$

A system will receive heat in a process if δQ > 0 ; the process will be adiabatic if δQ = 0. from the (10):

$$\delta Q\geq 0 \Leftrightarrow c_p p\,dV+c_V V\,dp\geq 0 \Leftrightarrow \frac{dp}{dV}\geq-\frac{c_p p}{c_V V}=-\gamma\frac{p}{V} \quad (11) \quad (\text{with } \gamma=\frac{c_p}{c_V})$$

The adiabatic slope will be the limit condition of the (10), i.e.

$$\frac{dp}{dV}=-\gamma\frac{p}{V} \Rightarrow V\,dp+\gamma p\,dV=0 \Rightarrow d(pV^\gamma)=0 \Rightarrow pV^\gamma=constant \quad (12)$$

(equation of adiabats).

The heat exchanged during a process depends on the slope of the corresponding pV curve:
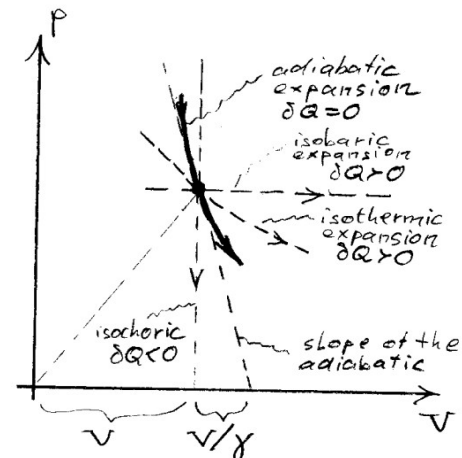during an expansion

$$\delta Q\geq 0 \Leftrightarrow \frac{dp}{dV}\geq\left[\frac{dp}{dV}\right]_{ad} \quad (11') \quad, \text{ with } \left[\frac{dp}{dV}\right]_{ad}=-\gamma\frac{p}{V}$$
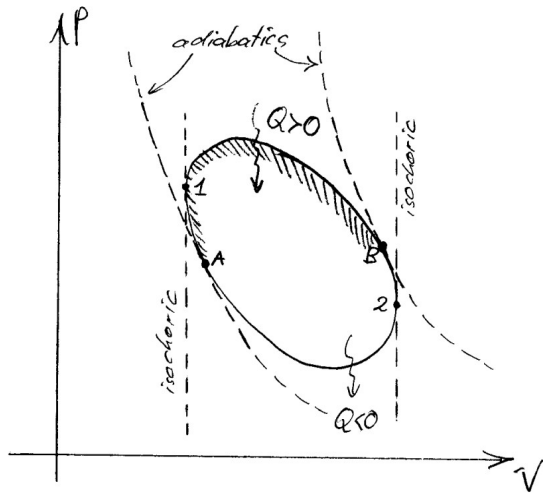
, i.e.
he heat exchange is positive if the slope of the expansion curve is (a number) greater than the slope of the adiabat in the same point; during a compression, the opposite is true, i.e.

$$\delta Q\geq 0 \Leftrightarrow \frac{dp}{dV}\leq\left[\frac{dp}{dV}\right]_{ad} \quad (11'').$$

which is summarised in the figure next.

4. Carnot's theorem

Let us consider a power reversible cycle (A → 1 → B → 2 → A), as in the figure next, where exchanges of heat are indicated, together with the two extreme tangent adiabats.
The shaded portion between the points A and B, delimited by the tangent adiabats, is the portion of the cycle where Q>0, the remaining portion is where Q<0; the upper portion between the points 1 and 2, delimited by tangent isochorics is the expansion phase (W>0), the lower portion between points 1 and 2 is the compression phase (W<0).

In Carnot's cycle heat is exchanged only at constant temperature and with only two heat sources, i.e. the cycle comprises two isotherms and two adiabats, as in the figure below.

The efficiency of this cycle is :

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{n\,R\,T_L \ln\frac{V_3}{V_4}}{n\,R\,T_H \ln\frac{V_2}{V_1}} \quad (12)$$

Along isotherms it will be also :

$$p_1 V_1 = p_2 V_2 \;;\; p_3 V_3 = p_4 V_4 \;\Rightarrow\; \frac{p_4}{p_3} = \frac{V_3}{V_4} \;;\; \frac{p_1}{p_2} = \frac{V_2}{V_1} \quad (12'),$$

and considering the equations of adiabatics:

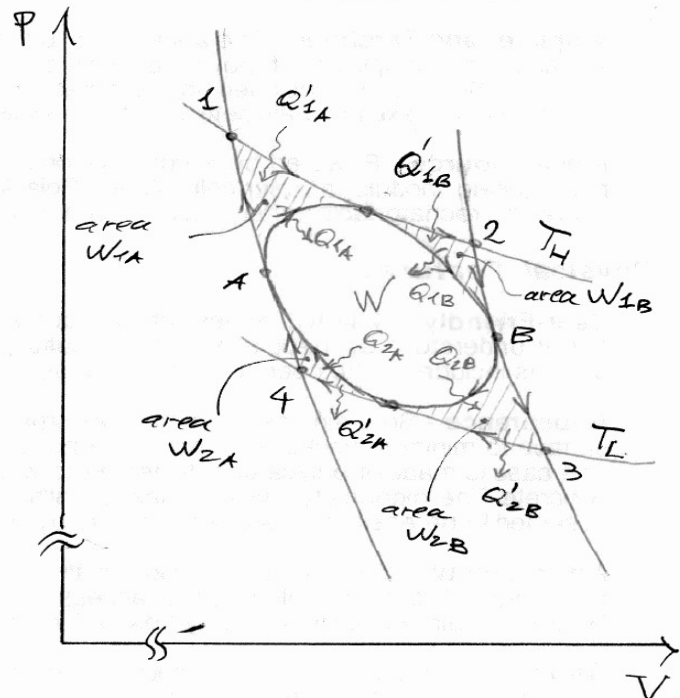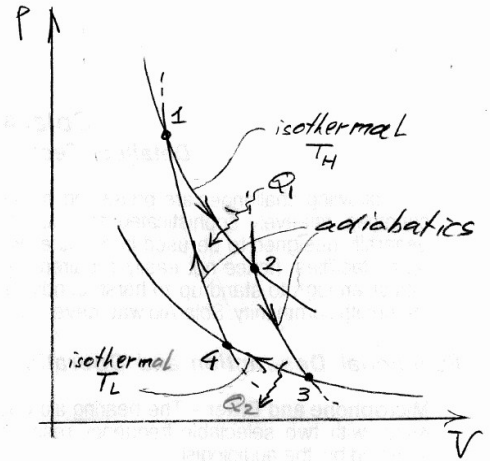$$p_1 V_1^\gamma = p_4 V_4^\gamma \;;\; p_2 V_2^\gamma = p_3 V_3^\gamma \;\Rightarrow\; \frac{p_1}{p_2}\left(\frac{V_1}{V_2}\right)^\gamma = \frac{p_4}{p_3}\left(\frac{V_3}{V_4}\right)^\gamma \quad (12'')$$

then, from the (12') and the (12") we come to the $\dfrac{V_2}{V_1} = \dfrac{V_3}{V_4}$ (12'''), and from the (12) we finally find Carnot's efficiency:

$$\eta = \eta_{Car} = 1 - \frac{T_L}{T_H} \quad (14)$$

It can now be proved that **if we consider a power reversible cycle represented by a closed curve in pV plane, for which a single heat input phase and a single heat output phase may be identified between two points A and B, its efficiency is lower or equal to Carnot efficiency between the highest and the lowest reached temperatures**.

Given such a cycle, let us consider the circumscribed Carnot's cycle, I.e. with isotherms and adiabats tangent to it (see figure next). Four

additional power cycles may be defined with processes from Carnot's cycle and from the given cycle, i.e.:
Cycle 1A (1 → mid of 1-2 → A → 1);
Cycle 1B (2 → B → mid of 1-2 → 2);
Cycle 2A (A → mid of 3-4 → 4 → A);
Cycle 2B (B → 3 → mid of 3-4 → B),
producing each a work corresponding to the respective enclosed area W_{1A}, W_{1B}, W_{2A}, W_{2B}. .
In cycles 1A and 1B the system receives respective heats Q'_{1A} and Q'_{1B}, whose sum is the heat absorbed by a system in Carnot's cycle along isotherm 1-2, and outputs respective heats Q_{1A} and Q_{1B}, whose sum is the heat received by the system in the heat input phase of the given cycle (due to reversibility of all processes, the process B → A delivers exactly the same heat that is received in the process A → B), i.e.

$$Q'_1 = Q'_{1A} + Q'_{1B} \; ; \; Q_1 = Q_{1A} + Q_{1B} \; .$$

Similarly, for cycles 2A and 2B it can be observed that in such cycles altogether the system receives the heat output during the given cycle in the heat output phase, and that they output altogether the heat output by the system in Carnot's isotherm 3-4 : $\quad Q'_2 = Q'_{2A} + Q'_{2B} \; ; \; Q_2 = Q_{2A} + Q_{2B}$. Since in a reversible cycle it is ΔU = 0, for the 1st law of thermodynamics we will have also:

$$Q'_{1A} = Q_{1A} + W_{1A} \; ; \; Q'_{1B} = Q_{1B} + W_{1B} \; ; \; Q_{2A} = Q'_{2A} + W_{2A} \; ; \; Q_{2B} = Q'_{2B} + W_{2B} \quad \text{and, in particular}$$
$$Q'_1 > Q_1 \; ; \; Q_2 > Q'_2 \quad \text{(6)}$$

From the (6) it follows that $\quad \dfrac{Q_2}{Q_1} > \dfrac{Q'_2}{Q'_1} \; \Rightarrow \; 1 - \dfrac{Q_2}{Q_1} < 1 - \dfrac{Q'_2}{Q'_1} \quad$, I.e. $\quad \eta \leq \eta_{Car} = 1 - \dfrac{T_L}{T_H} \quad$ (15)

(the equal relation being valid only if $W_{1A} = W_{1B} = W_{2A} = W_{2B} = 0$, I.e. if the cycles coincide).

If we now consider a general reversible power cycle, by drawing tangent adiabats and identifying their contact points (points A, B, C, D, E in the figure next) with the cycle, we can split the power cycle into partial cycles having each a single heat input phase and a single output phase defined by two points (e.g. cycle C → D → B → A → C in the next figure, having heat input from C to D, and cycle E → A → B → E having heat input from E to A), to which the previous result applies, i.e. for the k-th of these cycles it will be

$$\eta_k = \frac{W_k}{Q_{ik}} = 1 - \frac{T_{Lk}}{T_{Hk}} \quad \text{(16)} ,$$

the subdivision borders between the partial cycles being adiabats, without heat exchange. Furthermore the total work accomplished by the cycle will be the total enclosed area, i.e.
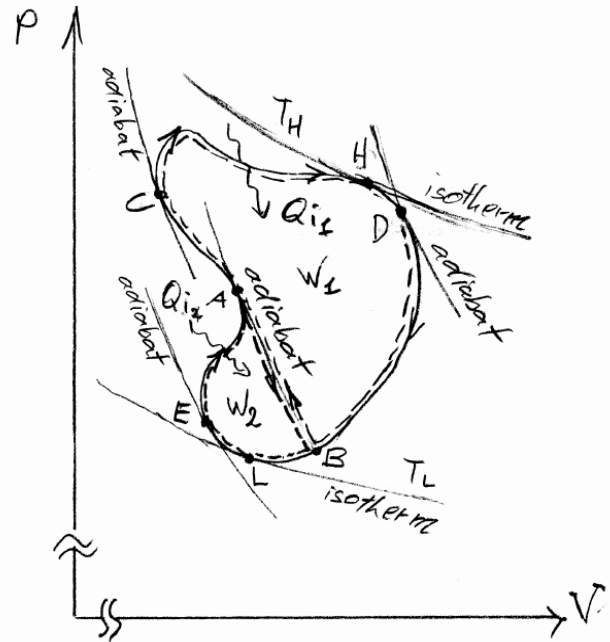

$W = \sum\limits_k W_k$, and the total input heat will be

$Q_i = \sum\limits_k Q_{ik}$. If we consider the highest and lower temperatures T_H and T_L reached in the

cycle, it will be: $\quad T_{Lk} \geq T_L \; ; \; T_{Hk} \leq T_H \; , \; \forall k \;$; hence $\quad \eta_k = 1 - \dfrac{T_{Lk}}{T_{Hk}} \leq 1 - \dfrac{T_L}{T_H} \; , \; \forall k \;$.

Finally we have $\quad \eta = \dfrac{W}{Q_i} = \dfrac{\sum\limits_k W_k}{\sum\limits_k Q_{ik}} = \dfrac{\sum\limits_k Q_{ik} \eta_k}{\sum\limits_k Q_{ik}} \leq \dfrac{\sum\limits_k Q_{ik}\left(1 - \dfrac{T_L}{T_H}\right)}{\sum\limits_k Q_{ik}} \; \Rightarrow \; \eta \leq 1 - \dfrac{T_L}{T_H} \;$, i.e. the **total**

efficiency of <u>any</u> generic cycle is not greater than Carnot efficiency between the highest and the lowest reached temperatures. (Carnot's theorem)

5. The 2ⁿᵈ law

Having proved Carnot's theorem, the 2ⁿᵈ law becomes just a direct consequence. E.g. let us consider a Carnot power engine between sources T_H and T_L, as in the figure next.

If heat transfer was possible from source T_L to source T_H without spending any work, we could combine a machine that performs such heat transfer with a Carnot power engine, to bring back a part Q'2 of Carnot's output heat to the hottest source. For such a resulting machine the actual input heat would be $Q_i = Q_1 - Q'_1 < Q_1$, and therefore

$$\eta = \frac{W}{Q_i} > \frac{W}{Q_1} = 1 - \frac{T_L}{T_H}$$, contrary to Carnot's theorem.

Therefore **it must be impossible to transfer heat from a lower temperature source to a higher temperature one without spending work.**

In the end, **for reversible processes involving an ideal gas, apparently we have come to the 2ⁿᵈ law in Clausius' formulation, starting only from the 1ˢᵗ law** (it would be easy to come similarly from Carnot's theorem to other formulations of the 2ⁿᵈ law).