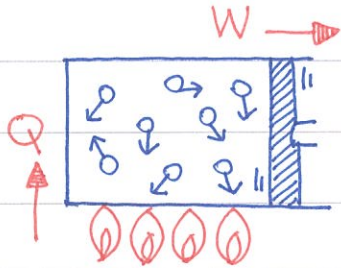# HH0103 Heat and the First Law of Thermodynamics

Consider heating some gas as shown below. From our intuition, it's expected that

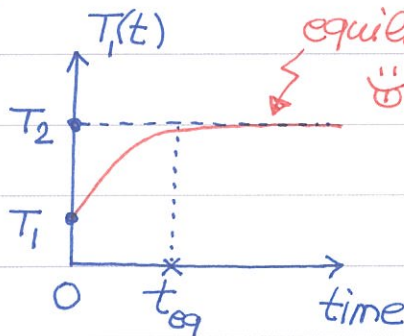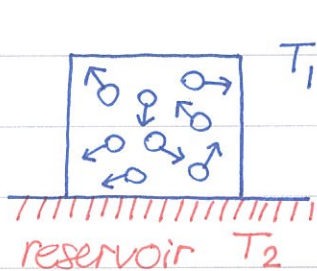$$Q = \Delta U + W \quad \leftarrow 1^{st} \text{ law of thermodynamics}$$

Q is the heat absorbed by the gas and W is the work done by the gas. Finally, ΔU is the change of the internal energy.

Consider two systems in thermal contact with $T_2 > T_1$. It is reasonable to guess how thermal equilibrium is reached. Suppose the thermal contact starts at $t=0$.

Because the reservoir is HUGE, T_2 remains constant. The temp. of the system $T_1(t)$ increases from T_1 to T_2 and reaches thermal equilibrium with the reservoir.

① Temperature. Let us try to understand how thermal equilibrium is reached from microscopic collisions between gas molecules. The systems can exchange energy by collisions. For simplicity, 1D (along z-axis) elastic collisions are considered here,
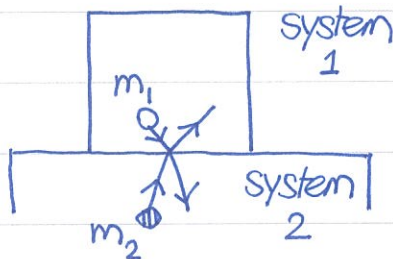
$$\upsilon_1' = \frac{m_1 - m_2}{m_1 + m_2} \upsilon_1 + \frac{2m_2}{m_1 + m_2} \upsilon_2 \quad \leftarrow \upsilon_2' \text{ can be computed too!}$$

The energy change due to collision is

$$\Delta u_1 = \frac{1}{2} m_1 \upsilon_1'^2 - \frac{1}{2} m_1 \upsilon_1^2 = \frac{4 m_1 m_2}{(m_1 + m_2)^2} \left[\frac{1}{2} m_2 \upsilon_2^2 - \frac{1}{2} m_1 \upsilon_1^2 + \frac{1}{2}(m_1 - m_2) \upsilon_1 \upsilon_2 \right]$$

Each collision leads to different Δu_1. On average,

$$\langle \Delta u_1 \rangle = \frac{4m_1 m_2}{(m_1+m_2)^2} \left[\langle \tfrac{1}{2}m_2 v_2^2 \rangle - \langle \tfrac{1}{2}m_1 v_1^2 \rangle \right]$$

The last term vanishes after taking average because $\langle v_1 v_2 \rangle = \langle v_1 \rangle \langle v_2 \rangle = 0$! When equilibrium is reached, we expect the average energy exchange vanishes,

$$\langle \Delta u_1 \rangle = 0 \; @ \text{ equilibrium} \longrightarrow \boxed{\langle \tfrac{1}{2}m_2 v_2^2 \rangle = \langle \tfrac{1}{2}m_1 v_1^2 \rangle}$$

Thus, it is tempting to define the temperature this way,

$$\boxed{\langle \tfrac{1}{2}m_i v_i^2 \rangle = \tfrac{1}{2}kT_i \;\; (i=1,2)} \longrightarrow T_1 = T_2 \quad \begin{array}{l} \text{equilibrium} \\ \text{criterion } \ddot{\smile} \end{array}$$

↑ Boltzmann constant.

From the definition of temperature, the energy change is

$$\boxed{\langle \Delta u_1 \rangle = \frac{4m_1 m_2}{(m_1+m_2)^2} \cdot \tfrac{1}{2}k(T_2-T_1) \propto (T_2-T_1)} \quad \begin{array}{l} \text{direction of} \\ \text{heat flow.} \end{array}$$

Let us find the dynamical equation for $T_1(t)$.

(a) According to the definition, $\langle u_1 \rangle = \langle \tfrac{1}{2}m_1 v_1^2 \rangle = \tfrac{1}{2}kT_1$

$$\left\langle \frac{du_1}{dt} \right\rangle = \tfrac{1}{2}k \frac{dT_1}{dt} \propto \frac{dT_1}{dt} \quad \text{energy flow} \propto \text{temp changing rate}$$

(b) From the above discussion, $\langle \Delta u_1 \rangle \propto (T_2-T_1)$,

$$\left\langle \frac{du_1}{dt} \right\rangle \propto (T_2-T_1) \qquad \left\{ \begin{array}{l} \text{Suppose system 2 is HUGE} \Rightarrow T_2 = \text{Const.} \\ \Delta T \text{ drives the energy flow.} \end{array} \right.$$

Combine (a) and (b) together and we arrive at

$$\boxed{\frac{dT_1}{dt} = \gamma(T_2-T_1)} \quad \text{Set } X = T_1 - T_2 \longrightarrow \frac{dX}{dt} = -\gamma X$$

It is straightforward to find the solution $X(t)$.

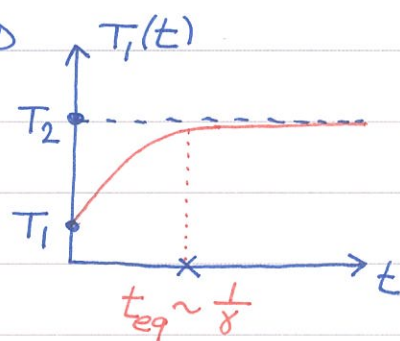$$X(t) = X(0) e^{-\gamma t} = -(T_2-T_1)e^{-\gamma t} \quad \longleftarrow X(0) = T_1 - T_2$$

The temperature of system 1 is

$$T_1(t) = T_2 - (T_2 - T_1)e^{-\gamma t}$$

It's easy (yet important) to check that $T_1(0) = T_1$ and $T_1(\infty) = T_2$ 😲 Quite interesting that $T_1(t)$ approaches thermal equilibrium in exponential form.

(graph showing $T_1(t)$ rising from T_1 to T_2 with $t_{eq} \sim \frac{1}{\gamma}$)

① **The First Law revisited.** Starting from work-energy theorem for a system, $\Delta K = W_{ex} + W_{in}$. If the internal forces are conservative, $W_{in} = -\Delta U_{in}$. In addition, the kinetic energy can be decomposed into two parts: $\Delta K = \Delta(\frac{1}{2}MU_{cm}^2 + K_{in})$. Combine all pieces together,

$$\Delta(\frac{1}{2}MU_{cm}^2 + K_{in} + U_{in}) = W_{ex}$$

contains both conservative and non-conservative!

$U_{cm} = 0$ internal energy.

Most of the time, $U_{cm} = 0$ and the energy conservation gives

$$\boxed{\Delta U = W_{ex}}$$

Notice that (diagram) $W_{ex} = -$ (diagram) W

Making use of the relation $W_{ex} = -W$, the E-conservation is

$$\boxed{\Delta U + W = 0}$$

↑ not quite right 😕

But, this is not quite the 1st law of thermodynamics. Something is missing....

There are some energy changes through microscopic collisions.

$$\boxed{W_{ex} = W_{micro} + W_{macro} = Q - W}$$

W_{micro} is due to molecular collisions at microscopic length scale without noticable changes in macroscopic variables. ⟶ HEAT 😵

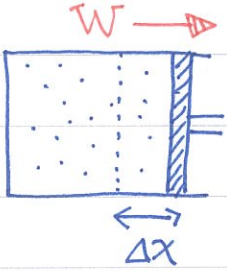Finally, we arrive at the 1st law of thermodynamics, hopefully, we now know temp T and heat Q better!

$$\Delta U = Q - W$$
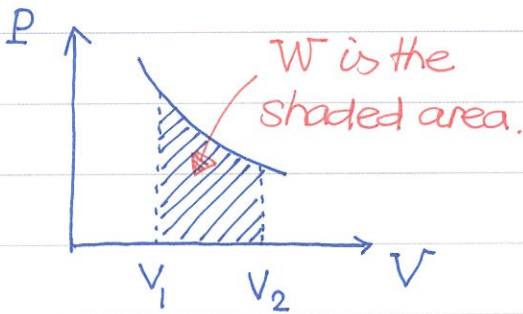
① Work. The work done by the system can be computed

$$W = F \cdot \Delta x = P \cdot A \Delta x$$
$$= P \Delta V = P(V_2 - V_1)$$

In general case, the pressure is not constant and the work turns into a definite integral. Let us try to compute the work W for ideal gas during isothermal expansion.

$$W = \int_{V_1}^{V_2} p \, dV$$

W is the shaded area.

$$W = \int_{V_1}^{V_2} p \, dV \quad \longleftarrow PV = NkT$$
$$= NkT \int_{V_1}^{V_2} \frac{dV}{V}$$

Carry out the integral to obtain W,

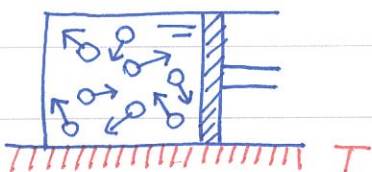$$W = NkT \ln V \Big|_{V_1}^{V_2} = NkT \ln\left(\frac{V_2}{V_1}\right)$$

what about ΔU and Q ?

Generalize our previous calculations to 3D for internal energy,

$$\langle u \rangle = \left\langle \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \right\rangle = \frac{3}{2} kT \quad \longrightarrow U = N\langle u \rangle = \frac{3}{2} NkT$$

Thus, $\Delta U = 0$ for ideal gas during isothermal expansion. From the 1st law, $Q = \Delta U + W = W$ here.

$$Q = W = NkT \ln\left(\frac{V_2}{V_1}\right)$$
$$\Delta U = 0 \quad \text{isothermal}$$

T

Ⓘ **Heat capacity.** The heat capacities of const volume and const pressure are defined as

$$C_P \equiv \frac{1}{n}\left(\frac{dQ}{dT}\right)_P \quad \& \quad C_V = \frac{1}{n}\left(\frac{dQ}{dT}\right)_V$$

Write the 1st law in differential form,

$$dQ = dU + P\,dV \longrightarrow \frac{dQ}{dT} = \frac{dU}{dT} + P\frac{dV}{dT}$$

(a) If the volume is fixed, $dV = 0$

$$\left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \longrightarrow \boxed{C_V = \frac{1}{n}\left(\frac{dU}{dT}\right)_V}$$

(b) If the pressure is fixed,

$$\left(\frac{dQ}{dT}\right)_P = \left(\frac{dU}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P \longrightarrow \boxed{C_P = \frac{1}{n}\left(\frac{dU}{dT}\right)_P + \frac{P}{n}\left(\frac{dV}{dT}\right)_P}$$

We are now ready to compute C_V, C_P for monoatomic ideal gas,

$$U = \frac{3}{2}NRT = \frac{3}{2}nRT \longrightarrow C_V = \frac{1}{n}\left(\frac{dU}{dT}\right)_V = \frac{1}{n}\cdot\frac{3}{2}nR$$
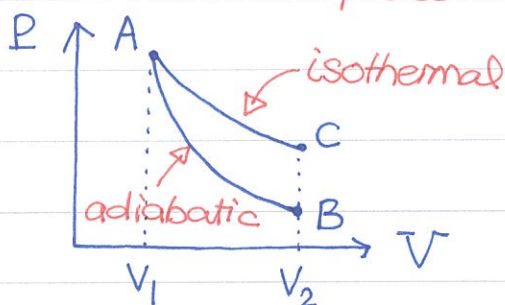
$$\longrightarrow \boxed{C_V = \frac{3}{2}R} \longleftarrow \text{very simple} \quad \odot\odot$$

Now let us turn to the calculation for C_P.

$$C_P = \frac{1}{n}\left(\frac{dU}{dT}\right)_P + \frac{P}{n}\left(\frac{dV}{dT}\right)_P = \frac{3}{2}R + \frac{P}{n}\cdot\frac{nR}{R} \qquad V = \frac{nRT}{P}$$

$$\longrightarrow \boxed{C_P = \frac{5}{2}R} \qquad \text{The ratio } \gamma \equiv \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} \quad \underline{universal.}$$

Ⓘ **Adiabatic process.** During adiabatic expansion ($Q=0$), the temp of the ideal gas decreases.

$$Q = 0 \Rightarrow \Delta U = -W < 0$$

T decreases!

For ideal gas, $dU = nC_V dT$. Because the process is adiabatic, $dU = d\cancel{Q} - pdV$. We obtain a simple differential relation, $\{ nC_V dT + pdV = 0 \}$ Starting from the equation of state, we obtain another differential relation,

$PV = nRT \longrightarrow \{ pdV + Vdp = nRdT \} \leftarrow$ eliminate dT

$nRC_V dT + RpdV = 0$

$C_p pdV + C_V Vdp - nRC_V dT = 0$ $\longrightarrow$ $P(C_V + R)dV + C_V Vdp = 0$

Note that $C_V + R = C_p$ for ideal gas. The above relation is

$$C_p \frac{dV}{V} + C_V \frac{dp}{P} = 0 \implies \boxed{\frac{dp}{P} + \gamma \frac{dV}{V} = 0} \quad \text{Yes!}$$

Integrate the differential relation,

$$\int_1^2 \frac{dp}{P} + \gamma \frac{dV}{V} = 0 \longrightarrow \ln\frac{P_2}{P_1} + \gamma \ln\frac{V_2}{V_1} = 0$$

Combine the logarithm to simplify the solution,

$$\ln\left(\frac{P_2 V_2^\gamma}{P_1 V_1^\gamma}\right) = 0 \implies \boxed{P_2 V_2^\gamma = P_1 V_1^\gamma = \text{const}}$$

Compared with $PV = \text{const}$ in isothermal process, the relation changes to $PV^\gamma = \text{const}$ in adiabatic process for ideal gas.

Now that we derive the relation $P = P(V)$, it is easy to calculate the work W:

$$W = \int_{V_1}^{V_2} pdV = \text{const.} \int_{V_1}^{V_2} V^{-\gamma} dV \quad \text{where } PV^\gamma = \text{const.}$$

$$= \text{const.} \frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma} \quad \leftarrow \text{const} = P_1 V_1^\gamma = P_2 V_2^\gamma$$

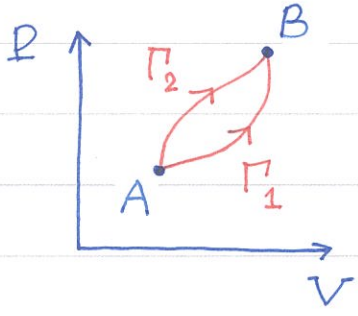$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{nR}{\gamma - 1}(T_1 - T_2)$$

what about ΔU ?

Note that $Q = 0 \Rightarrow$ We expect $\Delta U = -W$. Is it so? Let us calculate the change of internal energy,

$$\Delta U = nC_v (T_2 - T_1) \qquad \frac{nR}{\gamma - 1} = \frac{nRC_v}{C_p - C_v} = nC_v \ddot{\smile}$$

$$= \frac{nR}{\gamma - 1}(T_2 - T_1) \quad \longleftarrow \text{ just } -W, \text{ as expected.}$$

① Entropy.   Now we would like to introduce a peculiar thermodynamic variable — entropy.

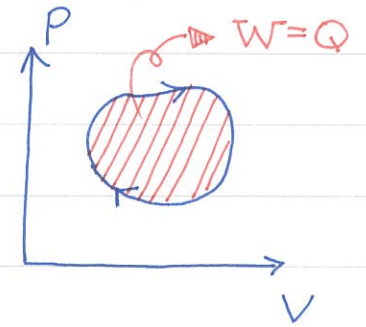Consider two different thermal processes along Γ_1 and Γ_2 from state A to B.

Clearly $W_1 = \int_{\Gamma_1} p \, dV \neq W_2 = \int_{\Gamma_2} p \, dV$

One also expects the absorbed heat $Q_1 \neq Q_2$ in general. However, because $\Delta U = U(B) - U(A)$ is independent of the paths, the 1st law gives $\Delta U = Q - W$

$\longrightarrow \boxed{Q_1 - W_1 = Q_2 - W_2}$ One can generalize the idea to a cycle.

Because the system returns to the original state, $\Delta U = 0$. Thus, $Q = W$ and

$$\boxed{Q = W = \oint p \, dV} \quad \longleftarrow \text{the enclosed area in P-V plane.}$$

In mathematical term, the above result means that

$$\oint dQ = Q \neq 0 \qquad dQ \text{ is not an exact differential and thus path dependent !}$$
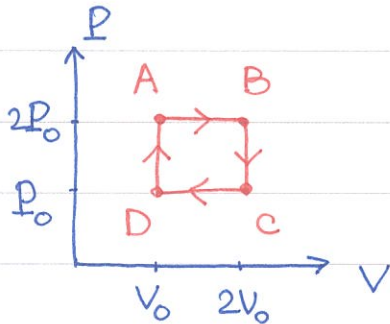
However, we would like to claim that

$$\oint \frac{dQ}{T} = 0$$ for ALL reversible cycles.

The proof is not easy and I shall skip it here. But, we can see how it works in simple cases. Consider the "square cycle" for ideal gas.

$$\Delta S_{A \to B} \equiv \int_A^B \frac{dQ}{T} = \int_A^B \frac{dU}{T} + \frac{PdV}{T}$$

$$= \int_A^B nC_V \frac{dT}{T} + nR \frac{dV}{V} \quad \Longleftarrow \text{ you will see } \ln \text{ again!}$$

Carry out the above integrals,

$$\Delta S_{A \to B} = nC_V \ln\left(\frac{T_B}{T_A}\right) + nR \ln\left(\frac{V_B}{V_A}\right) = nC_P \ln 2$$

Repeat the same calculation for $B \to C$,

$$\Delta S_{B \to C} = nC_V \ln\left(\frac{T_C}{T_B}\right) = -nC_V \ln 2 \quad \Longleftarrow \text{ no } \frac{P}{T}dV \text{ term because } V \text{ is fixed.}$$

Similarly, it is straightforward to complete the cycle,

$$\Delta S_{C \to D} = nC_V \ln\left(\frac{T_D}{T_C}\right) + nR \ln\left(\frac{V_D}{V_C}\right) = -nC_P \ln 2$$

$$\Delta S_{D \to A} = nC_V \ln\left(\frac{T_A}{T_D}\right) = nC_V \ln 2$$

Adding all pieces together, we find the sum is zero,

$$\oint \frac{dQ}{T} = \Delta S_{A \to B} + \Delta S_{B \to C} + \Delta S_{C \to D} + \Delta S_{D \to A}$$

$$= nC_P \ln 2 - nC_V \ln 2 - nC_P \ln 2 + nC_V \ln 2 = 0$$

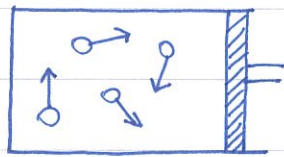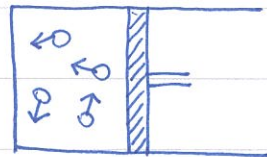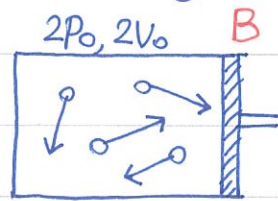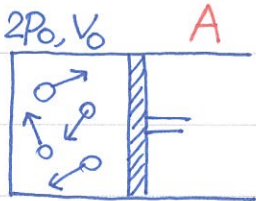$$\oint \frac{dQ}{T} = 0 \quad \text{as we claimed previously}$$

豪豬筆記

Because the integral for a complete cycle is zero, we can define a state function S as

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T}$$

S is the entropy.

It is fun to go back to the demo example.

2Po, Vo   A

2Po, 2Vo   B

Po, Vo   D

Po, 2Vo   C

$S(B) - S(A) = nC_p \ln 2$

$S(C) - S(B) = -nC_v \ln 2$

$S(D) - S(C) = -nC_p \ln 2$

$S(A) - S(D) = nC_v \ln 2$

From the above relations, one can express entropies with respect to the initial state A. Note that $T_A = T_C$ here.

$$S(B) = S(A) + nC_p \ln 2$$
$$S(C) = S(A) + nR \ln 2$$
$$S(D) = S(A) - nC_v \ln 2$$

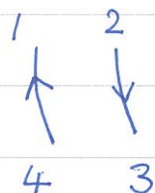$S(B) > S(C) > S(A) > S(D)$

Although it is hard to pin down the meaning of entropy S, it seems related to the "degree of disorder" in the system ☺

① Carnot cycle.   Consider a cycle consists of two isothermal and two adiabatic processes as shown on the left. The cycle is named after Carnot for his ingenious insight of heat engine and thermodynamics.
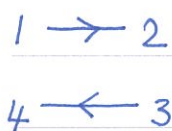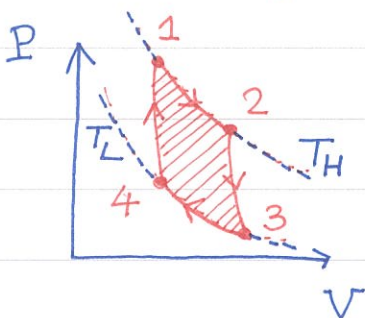
$1 \rightarrow 2$ isothermal
$4 \leftarrow 3$

1 ↑   2 ↓   adiabatic
4   3

let us compute
$W, Q, S \ldots$

Start with the work, W_{12}, W_{23}, W_{34}, W_{41}.

$$W_{12} = \int_1^2 P\,dV = nRT_H \int_1^2 \frac{dV}{V} = nRT_H \ln\frac{V_2}{V_1} > 0$$

We already compute the work done in the adiabatic process in previous section,

$$W_{23} = \frac{nR}{\gamma-1}(T_H - T_L) = nC_V(T_H - T_L) > 0$$

Similarly, one can obtain W_{34}, W_{41},

$$W_{34} = nRT_L \ln\left(\frac{V_4}{V_3}\right) \quad \text{and} \quad W_{41} = nC_V(T_L - T_H) < 0$$

We can rewrite W_{34} for easier comparison.

$$\begin{aligned} P_1 V_1 &= P_2 V_2 \\ P_3 V_3 &= P_4 V_4 \end{aligned} \longrightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}, \quad \frac{V_4}{V_3} = \frac{P_3}{P_4} \longrightarrow \frac{V_2 V_4}{V_1 V_3} = \frac{P_1 P_3}{P_4 P_2}$$

Now make use of the relations for adiabatic processes,

$$\begin{aligned} P_2 V_2^\gamma &= P_3 V_3^\gamma \\ P_4 V_4^\gamma &= P_1 V_1^\gamma \end{aligned} \longrightarrow \frac{V_2^\gamma}{V_3^\gamma} = \frac{P_3}{P_2}, \quad \frac{V_4^\gamma}{V_1^\gamma} = \frac{P_1}{P_4} \longrightarrow \left(\frac{V_2 V_4}{V_1 V_3}\right)^\gamma = \frac{P_1 P_3}{P_4 P_2}$$

Combine both sets of relations together,

$$\frac{V_2 V_4}{V_1 V_3} = \left(\frac{V_2 V_4}{V_1 V_3}\right)^\gamma \longrightarrow \left(\frac{V_2 V_4}{V_1 V_3}\right)^{\gamma-1} = 1 \longrightarrow \boxed{\frac{V_2 V_4}{V_1 V_3} = 1}$$

Now we are ready to rewrite the work W_{34},

$$W_{34} = nRT_L \ln\left(\frac{V_4}{V_3}\right) = -nRT_L \ln\left(\frac{V_2}{V_1}\right) < 0$$

The total work done for a complete cycle is

$$W = \oint P\,dV = W_{12} + W_{23} + W_{34} + W_{41}$$

$$= nRT_H \ln\left(\frac{V_2}{V_1}\right) + nC_V(T_H - T_L) - nRT_L \ln\left(\frac{V_2}{V_1}\right) + nC_V(T_L - T_H)$$

$$\longrightarrow \boxed{W = nR(T_H - T_L)\ln\frac{V_2}{V_1}}$$

The system absorbs heat $Q_{in} = W_{12}$ @ temp T_H
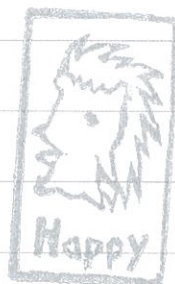and emits heat $Q_{out} = W_{34}$ @ temp T_L.

$$Q_{in} = W_{12} = nRT_H \ln \frac{V_2}{V_1} > 0$$

$$Q_{out} = W_{34} = -nRT_L \ln \frac{V_2}{V_1} < 0$$

It shall be easy to see that Q_{in} and Q_{out} are related,

$$\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_L} = 0 \quad \rightarrow \quad \oint dS = \oint \frac{dQ}{T} = \frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_L} = 0 \, !$$

Once again, we demonstrate that $\oint dQ/T = 0$, i.e. the entropy S only depends on the state.

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2013.1224

Happy