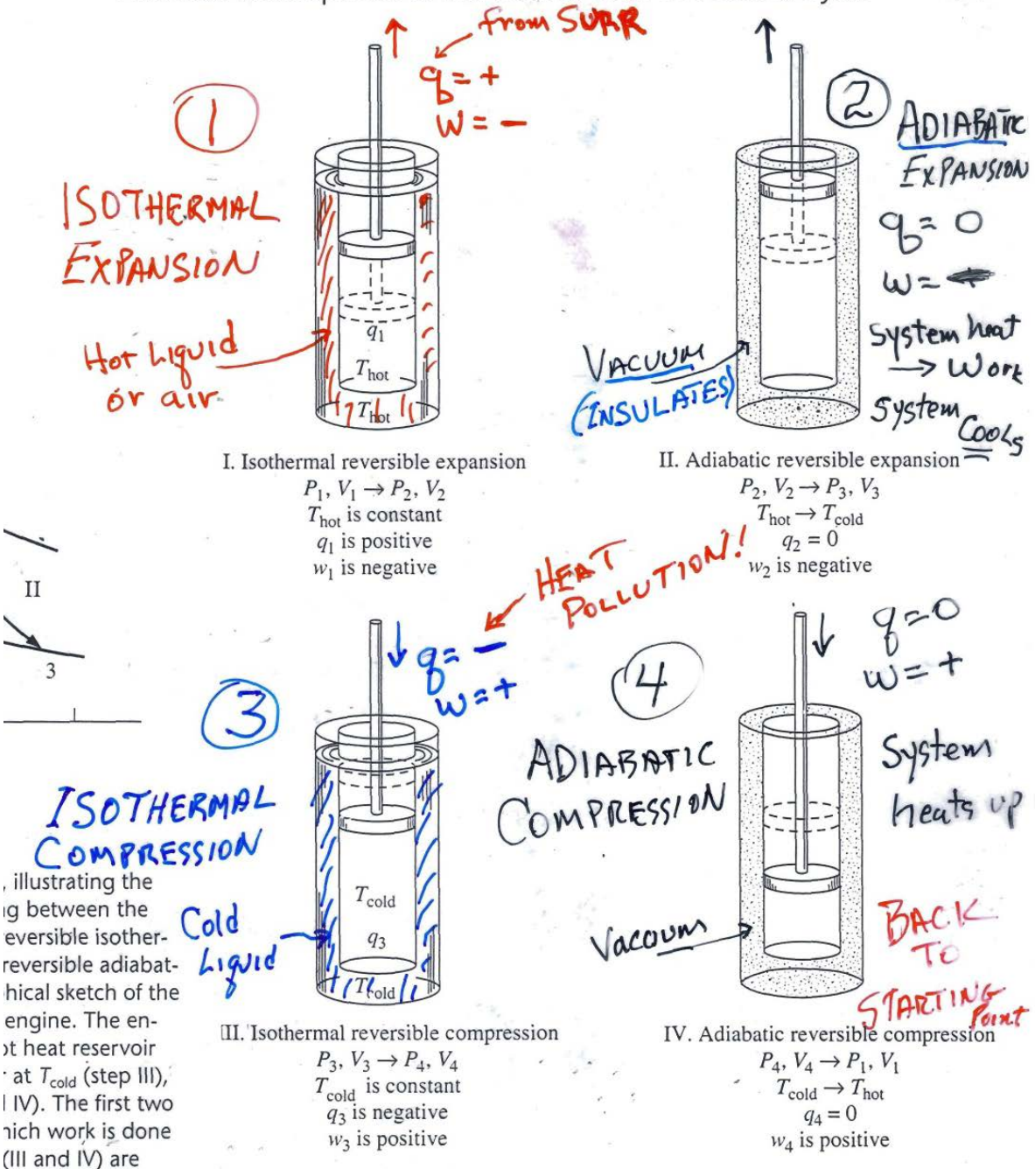
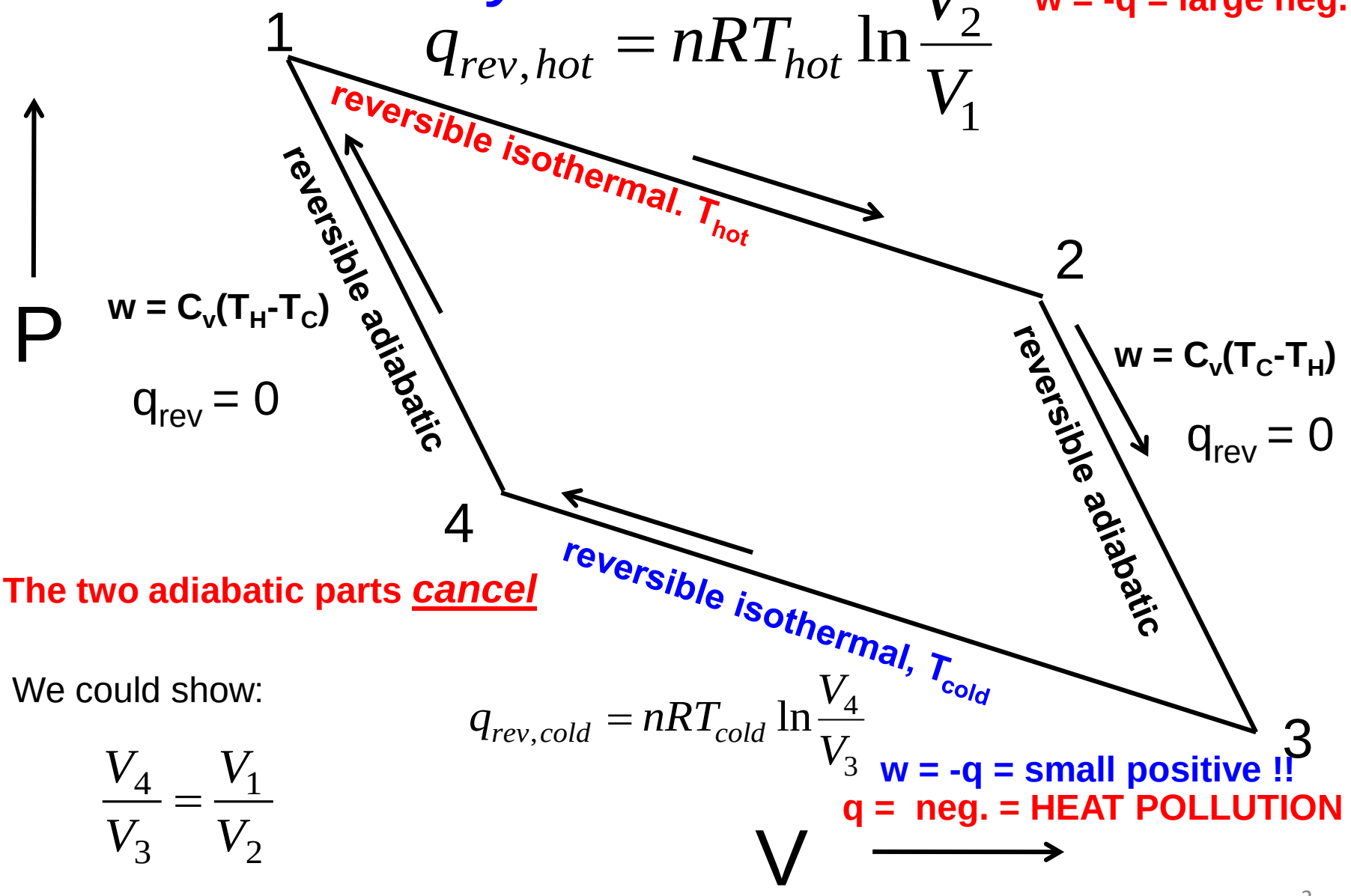
Fig. 3.2



, illustrating the
ıg between the
eversible isother-
reversible adiabat-
hical sketch of the
engine. The en-
ɔt heat reservoir
at T_{cold} (step III),
IV). The first two
nich work is done
(III and IV) are

Carnot's Cycle



$$q_{rev,hot} = nRT_{hot} \ln \frac{V_2}{V_1}$$

w = -q = large neg.

The two adiabatic parts *cancel*

We could show:

$$\frac{V_4}{V_3} = \frac{V_1}{V_2}$$

$$q_{rev,cold} = nRT_{cold} \ln \frac{V_4}{V_3}$$

w = -q = small positive !!

q = neg. = HEAT POLLUTION

$$\frac{\text{Net work out}}{\text{Heat from hot reservoir}} = \frac{nR\mathbf{T}_{\text{hot}} \ln \frac{V_2}{V_1} + nR\mathbf{T}_{\text{cold}} \ln \frac{V_4}{V_3}}{nR\mathbf{T}_{\text{hot}} \ln \frac{V_2}{V_1}}$$

$$\frac{V_4}{V_3} = \frac{V_1}{V_2} \qquad \ln \frac{V_4}{V_3} = \ln \frac{V_1}{V_2} = -\ln \frac{V_2}{V_1}$$

$$\frac{\text{Net work out}}{\text{Heat from hot reservoir}} = \frac{nR\mathbf{T}_{\text{hot}} \ln \frac{V_2}{V_1} - nR\mathbf{T}_{\text{cold}} \ln \frac{V_2}{V_1}}{nR\mathbf{T}_{\text{hot}} \ln \frac{V_2}{V_1}}$$

CANCEL $nR \ln \frac{V_2}{V_1}$

$$= \frac{\mathbf{T}_{\text{hot}} - \mathbf{T}_{\text{cold}}}{\mathbf{T}_{\text{hot}}} = \text{maximum efficiency of any heat energy}$$

The HEAT ENGINE runs spontaneously if HEAT is SUPPLIED

QUESTIONS:

What is ΔG for 1 CYCLE of the system?

Answer: ΔG for 1 CYCLE = 0 G is a state function, and applies only to the system;

Note that when ***useful*** work is involved, ΔG does not have to be negative for a spontaneous processes

What is the spontaneous process that we are harnessing here?

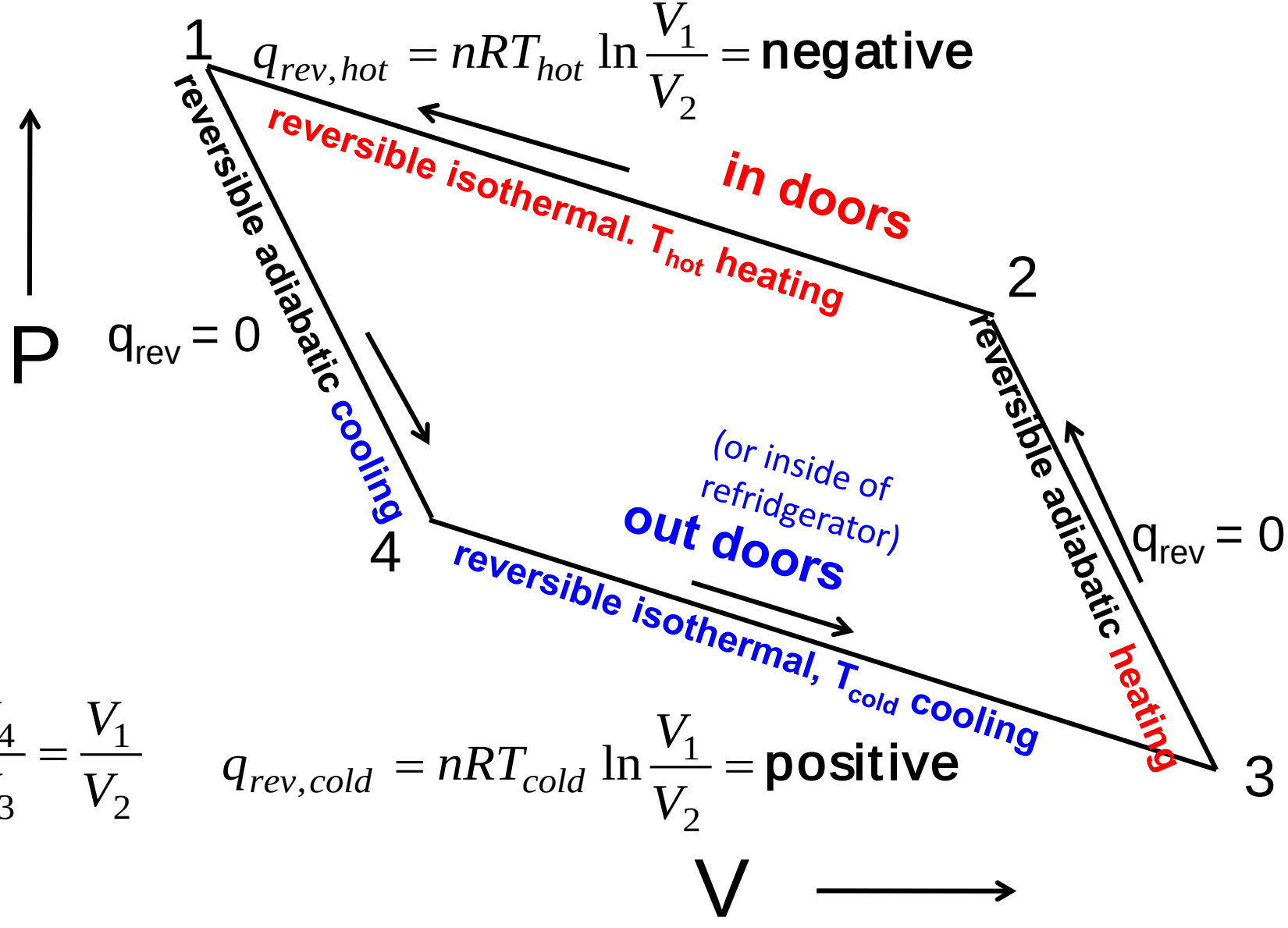
Answer: The flow of heat from a hot place to a cooler place

Reversible processes CAN BE REVERSED!

What do we call this engine if WORK is SUPPLIED instead of heat ?

Answer: A refrigerator, air conditioner, or heat pump, depending on whether we are pumping heat from a small place in a building, pumping heat out of the whole building, or warming the building by pumping heat into the building ***from*** the cold outside air.

Reversed Carnot's Cycle is a HEAT PUMP



As for the heat engine, for the *heat pump* what is valuable is q_{hot} , but now it is negative. Heat and work trade places. The efficiency is simply turned upside down.

$$\frac{\text{Heat } \textit{into} \text{ warm house}}{\text{Net work } \textit{from} \text{ electricity}} = \frac{nR\mathbf{T}_{\mathbf{hot}} \ln \frac{V_1}{V_2}}{nR\mathbf{T}_{\mathbf{hot}} \ln \frac{V_2}{V_1} - nR\mathbf{T}_{\mathbf{cold}} \ln \frac{V_3}{V_4}}$$

$$= \frac{\mathbf{T}_{\mathbf{hot}}}{\mathbf{T}_{\mathbf{hot}} - \mathbf{T}_{\mathbf{cold}}} = \frac{300}{300-270} = \frac{300 \text{ J of heat}}{30 \text{ J of electricity}}$$

Really??? **YES!!**

THE BIRTH OF ENTROPY (a new state function)

$$\frac{\text{Net work out}}{\text{Heat from hot reservoir}} = \frac{nR\mathbf{T}_{\text{hot}} \ln \frac{V_2}{V_1} - nR\mathbf{T}_{\text{cold}} \ln \frac{V_2}{V_1}}{nR\mathbf{T}_{\text{hot}} \ln \frac{V_2}{V_1}}$$

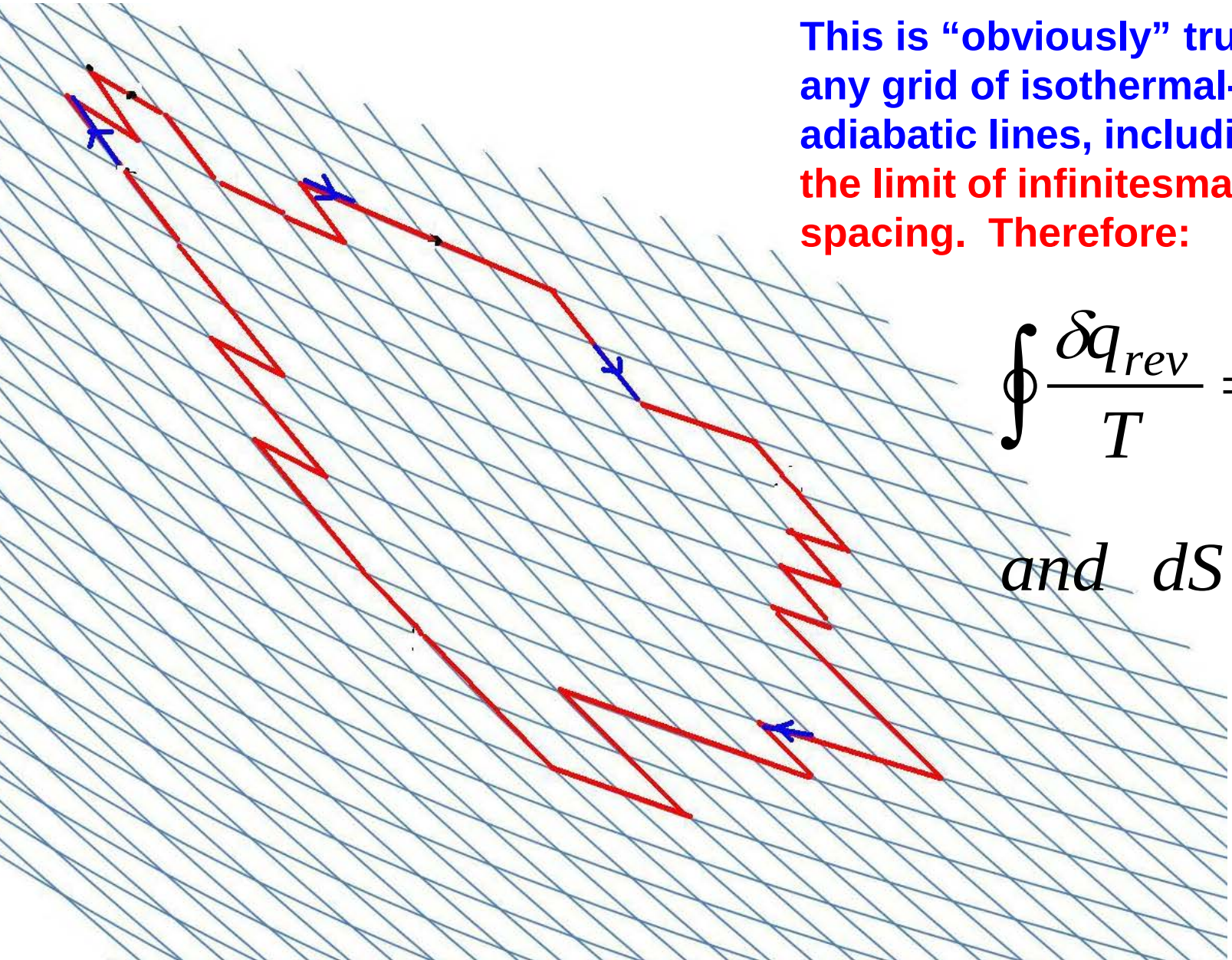
$$= \frac{\mathbf{T}_{\text{hot}} - \mathbf{T}_{\text{cold}}}{\mathbf{T}_{\text{hot}}} = \text{maximum efficiency of any heat energy}$$

But, Clausius and others 25 years later (~1850) noticed something important:

$$\sum_{cycle} \frac{q_{rev}}{T} = nR \frac{\mathbf{T}_{\text{hot}}}{\mathbf{T}_{\text{hot}}} \ln \frac{V_2}{V_1} + nR \frac{\mathbf{T}_{\text{cold}}}{\mathbf{T}_{\text{cold}}} \ln \frac{V_1}{V_2} + 0 + 0$$

$$= \text{ZERO!}$$

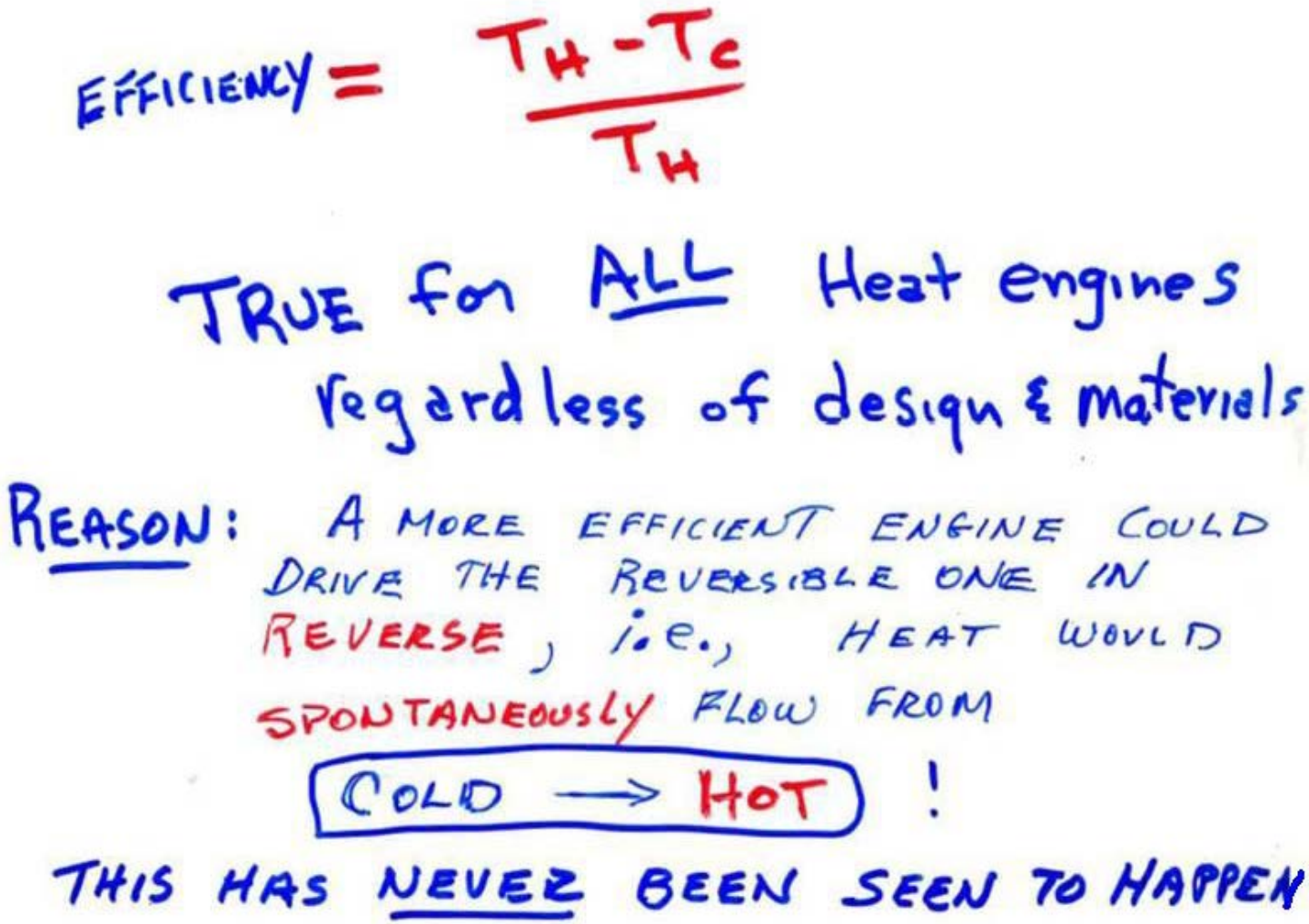
Suggesting that q_{rev}/T = change in a STATE FUNCTION



This is "obviously" true for any grid of isothermal-adiabatic lines, including in the limit of infinitesmal spacing. Therefore:

$$\oint \frac{\delta q_{rev}}{T} = 0,$$

$$and \;\; dS = \frac{\delta q_{rev}}{T}$$



That would be a **violation of the Zeroth Law of Thermodynamics:**

The "People's Law" .

All people who ever lived are the scientists who established this "Law".

ENTROPY ≡ S = State Variable

$$dS = \frac{dq_{rev}}{T} \quad \frac{J}{K} \text{ units}$$

or $\frac{cal}{K}$ "entropy unit"

$$\Delta S = \int \frac{dq_{rev}}{T}$$

$$\rightarrow \frac{q_{rev}}{T} \quad \text{if T Constant}$$

Efficiency of Heat Engine = $\frac{W_{HOT} + W_{COLD}}{q_{HOT}}$

$= \frac{T_{HOT} - T_{COLD}}{T_{HOT}}$

Our Best Steam Turbines

$T_{HOT} = 1000\,K$, $T_{COLD} = 400K$

Eff. $= \frac{1000 - 400}{1000} = 60\%$

What is the efficiency of the HEAT ENGINE that DRIVES LIFE ON EARTH???

Sun → Earth → Space

Efficiency = (6000-3) / 6000 = 0.9995 = **99.95%**

STATEMENTS of the SECOND LAW of THERMODYNAMICS

For reversible process $\Delta S + \Delta S_{surr} = 0$

One can show that if a process is done irreversibly, i.e.,
for ALL REAL PROCESSES,

more heat is delivered to surroundings than if done reversibly,

This means $\Delta S + \Delta S_{surr} > 0$ for all real processes
or $\Delta S_{universe} > 0$

We calculate ΔS_{surr} with the equation $\mathbf{\Delta S_{surr} = -q/T}$

If we calculate for a process that $\Delta S_{univ} < 0$ then it is **IMPOSSIBLE!**

Alternate statement:

It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work with the system ending in the same state in which it began. We call this the 'engine' statement of the second law.

Old Exam 1 Question

State A → State B Isothermal T = 400 K

Path 1 irreversible $q = 12000\ J$

Path 2 reversible $q = 8000\ J$

a) What is ΔS for path 1? ? 8000/400=20

b) What is ΔS for path 2? 8000/400=20

c) What is ΔS_{surr} for path 1? -12000/400= -30

d) What is ΔS_{surr} for path 2? -8000/400= -20

e) What is $\Delta S_{universe}$ for path 1 20-30=**-10**
(Is this path possible?) NOOOO

f) ΔS_{univ} for path 2? 0