

**Boiling Point** : when applied Pressure = “Vapor Pressure”

**But Why???**

First: What *is* boiling?

What will happen if you heat water that has no bubbles?

**The temperature will rise many degrees above the the boiling point!!**

i.e., it will “superheat”. But there will be **no boiling!**

When a particle of dust (containing air) falls in, the water will boil violently.

**Boiling is when liquid evaporates into bubbles and they rise to the surface. This requires  $V.P. > p_{ext}$**

(if V.P. *exactly* =  $p_{ext}$  , bubbles can exist but **will not grow**)

**Where do the bubbles come from?**

Dissolved gases are less soluble in hot water than in cold.

**Why do they persist during boiling?**

When a growing bubble detaches, part of it stays behind attached to the bottom of the vessel.

# The Second Law: The Entropy of the Universe Increases Always!

$$\Delta S + \Delta S_{\text{surr}}$$

$k = \text{Boltzmann constant} = R/\text{Avogadro's number}$   
units of  $\text{J molecule}^{-1} \text{K}^{-1}$

## Concepts

Water does not flow spontaneously up a waterfall to enlarge a pool at the top, and a candle never assembles a column of wax out of thin air by burning in reverse. Expressing this intuition of the direction of natural processes in objective and precise language is the domain of the Second Law of Thermodynamics.

The Second Law plays a crucial role in the discovery of a new variable of state, the entropy  $S$ , which is recognized as a measure of the disorder of the system, although the terms *disorder* and *order* do not capture the true meaning of entropy that was discovered by Ludwig Boltzmann (see sidebar). In an isolated system (which exchanges neither energy nor matter with the surroundings), every change of the system *increases* its entropy. If the system is not isolated from the surroundings, then the entropy of the system can decrease provided there is a larger increase in entropy of the surroundings. Thus, an elegant restatement of the Second Law emerges: the entropy of the universe—the system plus the surroundings—always increases.

An additional variable of state, the Gibbs free energy  $G$ , can be defined as the enthalpy  $H$  minus the product  $TS$ . The Gibbs energy always *decreases* in a process that occurs spontaneously at constant temperature and pressure, important conditions for biochemical processes. By calculating a free-energy change for a reaction, we can tell if the reaction proceeds spontaneously at constant temperature and pressure.

## The Third Law →

$$S = k \ln W$$

Inscribed on Ludwig Boltzmann's tombstone in Vienna is the equation  $S = k \ln W$ , meaning entropy is proportional to the logarithm of the number of different ways  $W$  a system can be rearranged without perceptibly changing it. Entropy had already been defined as a thermodynamic variable of state, but Boltzmann gave it a statistical meaning.

**$W$  = the number of microstates available to the system:  
a measure of DISORDER**

# Chapter 3: The Second Law

## Concepts:

Entropy, **S**, is a state function which is a measure of DISORDER

In an isolated system, **entropy increases** (if it can) until equilibrium is reached

## 2<sup>nd</sup> Law of Thermodynamics

$\Delta S + \Delta S_{\text{surr}} > 0$  for any actual process (spontaneously happening)

$\Delta S + \Delta S_{\text{surr}} = 0$  during equilibrium

$\Delta S$  may be calculated from  $dS = \frac{dq_{\text{rev}}}{T}$ ,  $\Delta S = \int dS$

If  $\Delta S + \Delta S_{\text{surr}}$  is calculated to be  $< 0$  (negative) the process **IS IMPOSSIBLE!**

We call  $\Delta S + \Delta S_{\text{surr}} = \Delta S_{\text{universe}}$

*The Third Law gives us **Absolute** entropies*

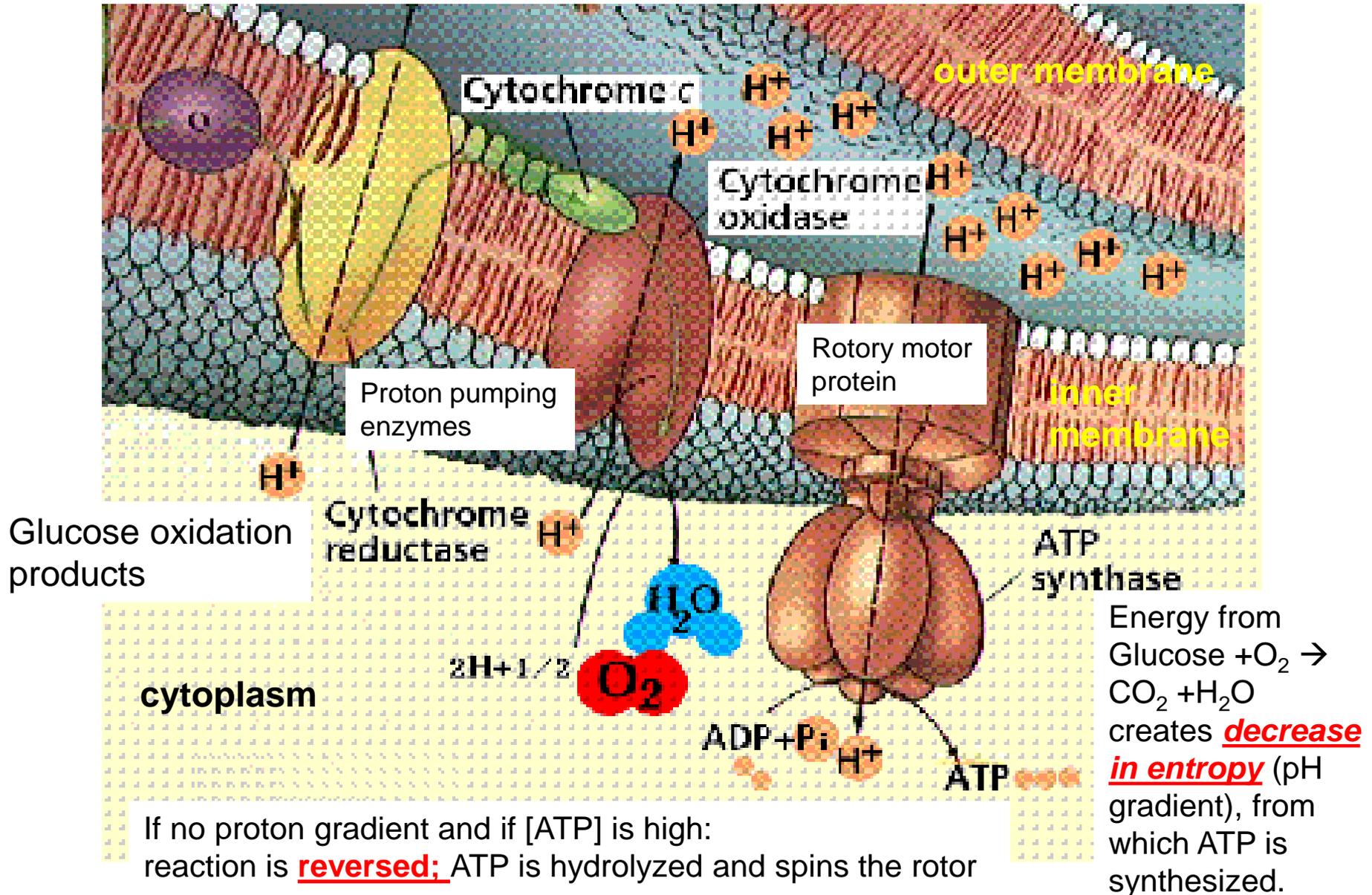
**TABLE A.5 Inorganic Compounds\***



**G = H-TS**

	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta_f G^\circ$ (kJ mol <sup>-1</sup> )
Ag(s)	0	42.55	0
Ag <sup>+</sup> (aq)	105.79	73.45	76.80
AgCl(s)	-127.01	96.25	109.77
C(g)	716.68	158.21	669.21
C(s, graphite)	0	5.74	0
C(s, diamond)	1.90	2.38	2.90
Ca(s)	0	41.42	0
CaCO <sub>3</sub> (s, calcite)	-1206.92	92.90	-1128.79
Cl <sub>2</sub> (g)	0	223.18	0
Cl <sup>-</sup> (aq)	-167.16	56.5	-131.23
CO(g)	-110.52	197.78	-137.01
CO <sub>2</sub> (g)	-393.51	213.85	-394.36
CO <sub>2</sub> (aq)	-413.80	117.6	-385.98

# Mitochondrion Has two membranes like bacteria

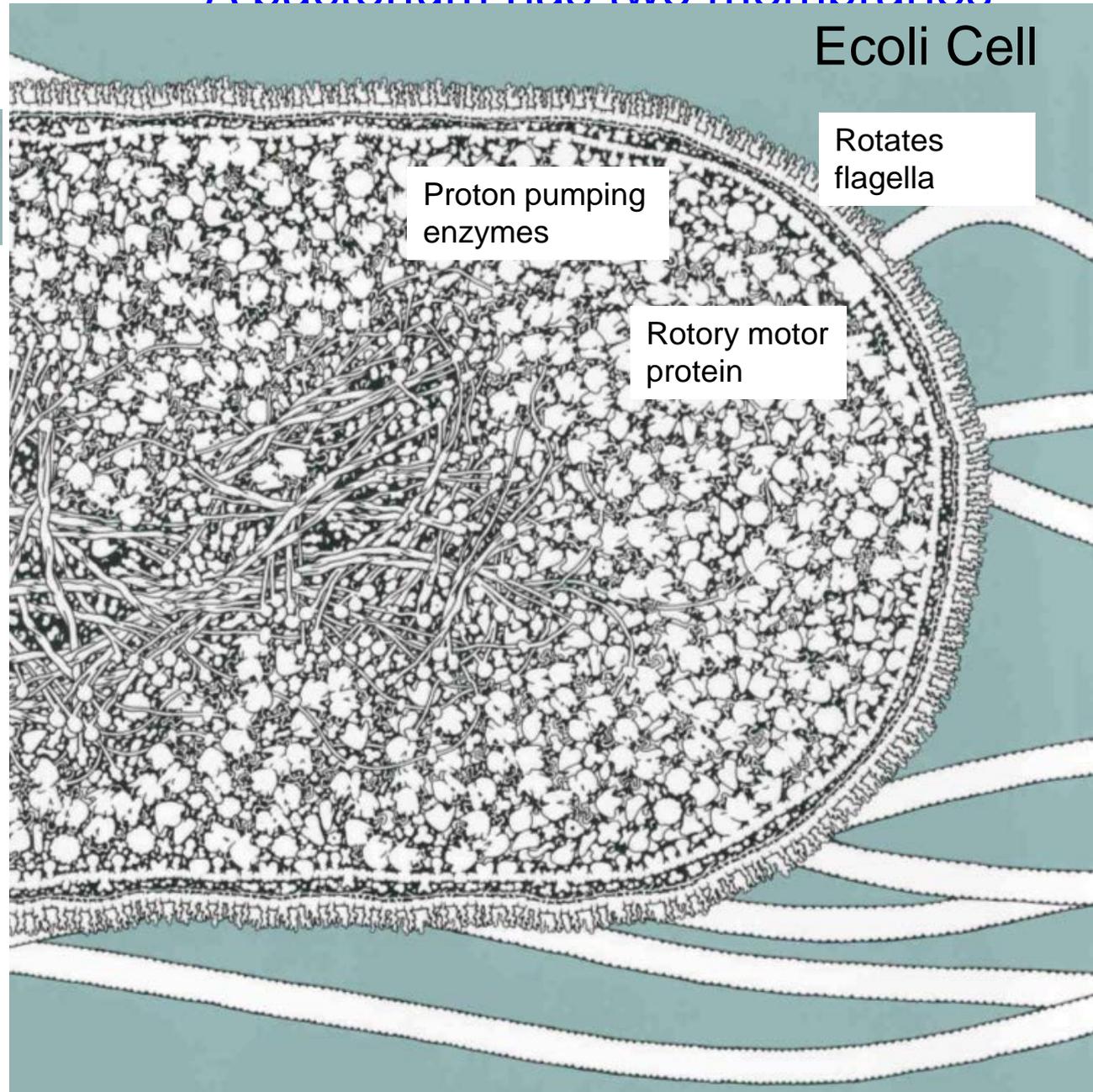


# A bacterium has two membranes

## Ecoli Cell

**The Machinery  
of Life**

David S. Goodsell



## THE ADJACENT POSSIBLE

A Talk with [Stuart A. Kauffman](#) [11.9.03]

*Refers to complexity of organic chemistry: Once a molecule is made, it is always possible to add another atom or two.*

*“An autonomous agent\* is something that can both reproduce itself and do at least one thermodynamic work cycle.”*

*“It turns out that this is true of all free-living cells, excepting weird special cases. They all do work cycles, **just like the bacterium spinning its flagellum** as it swims up the glucose gradient. The cells in your body are busy doing work cycles all the time.”*

***Kauffman while speaking here at MSU to the whole campus then proceeded to talk for 30 min on the Carnot Cycle***

<https://edge.org/conversation/the-adjacent-possible>

*(Chmy 361 students and a couple of physicists were the only people present who had any clue what he was talking about.)*

# [http://en.wikipedia.org/wiki/Nicolas\\_Leonard\\_Sadi\\_Carnot](http://en.wikipedia.org/wiki/Nicolas_Leonard_Sadi_Carnot)



Nicholas Leonard Sadi Carnot  
(1796-1832)

Nicolas Léonard Sadi Carnot (1796-1832) in the dress uniform of a student of the [École Polytechnique](#).

Born 1 June 1796(1796-06-01)  
[Palais du Petit-Luxembourg, Paris, France](#)

Died 24 August 1832 (aged 36)  
[Paris, France](#)

Residence [France](#)

Nationality [French](#)

Fields [Physicist](#) and [engineer](#)

Institutions [French army](#)

[Alma mater](#)  
[École Polytechnique](#)  
[École Royale du Génie](#)  
[Sorbonne](#)  
[Collège de France](#)

Academic advisors  
[Siméon Denis Poisson](#)  
[André Marie Ampère](#)  
[Dominique François Jean Arago](#)

Known for  
[Carnot cycle](#)  
[Carnot efficiency](#)  
[Carnot theorem](#)  
[Carnot heat engine](#)

Influenced  
[Benoît Paul Émile Clapeyron](#)  
[Rudolf Julius Emmanuel Clausius](#)

## Notes

He was the brother of [Hippolyte Carnot](#), his father was the mathematician [Lazare Carnot](#), and his nephews were [Marie François Sadi Carnot](#) and [Marie Adolphe Carnot](#).

# Excerpts from “*The Second Law*” by P. W. Atkins

“War and the steam engine joined forces and forged what was to become one of the most delicate of concepts [**the Second Law**]”

Sadie Carnot was an **engineer**, and the son of a famous mathematician, who was also a minister of war under Napoleon.

**Carnot fought against England in 1814.**

After France lost that war, Carnot perceived that if France could develop a more efficient steam engine, **it would rule the world.**

From Wikipedia:

“Carnot sought to answer two questions about the operation of heat engines: **“Is the work available from a heat source potentially unbounded?”**

and **“Can heat engines in principle be improved by replacing the steam with some other working fluid or gas?”** He attempted to answer these in a memoir, published as a popular work in 1824 when he was only 28 years old. It was entitled *Réflexions sur la puissance motrice du feu* (**“Reflections on the Motive Power of Fire”**). “

Published in 1824, this work was largely overlooked until Clausius recognized it as containing the key message of the 2<sup>nd</sup> Law in 1850.

The entire concept evolved from a simple hypothetical heat engine now known as the Carnot Cycle.

From its simple reversible isothermal and adiabatic expansions and compressions of an ideal gas,

Carnot elegantly proved that the theoretical maximum efficiency of any heat engine is given only by the fractional difference of the temperatures involved in the heat flow:

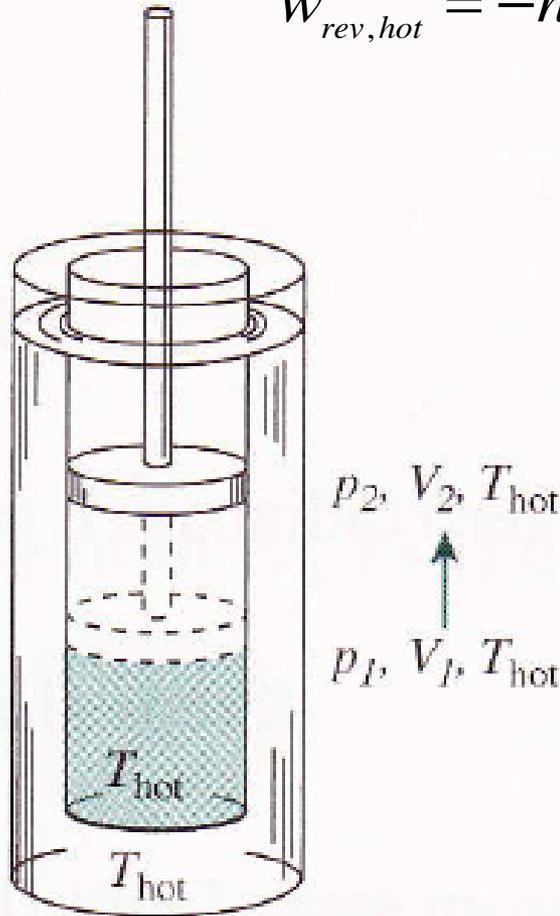
$$\frac{\text{Net work out}}{\text{Heat from hot reservoir}} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$

The dream of powering a ship in the ocean solely from the heat of the ocean was shattered!

The spontaneous flow of heat from hot → cold is partially harnessed to give work only if there is a temperature difference.

Isothermal reversible expansion of IDEAL GAS:  $\Delta U = 0$   $w = -q$

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



100 % of heat  $\rightarrow$  work  
but when piston reaches the top,

**THEN WHAT?**

**Returning to starting point:**

Isothermal reversible compression  
 $w = +$   $q = -$

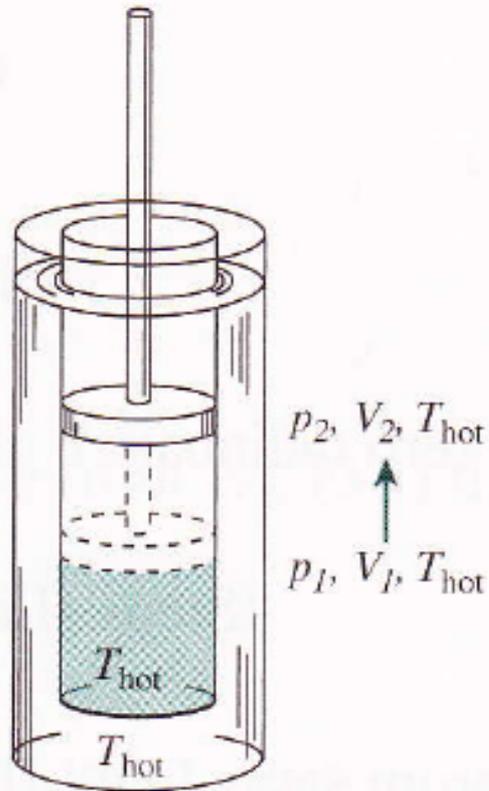
Requires putting the same  
work back and getting the  
heat back

Useful in B-B guns, but **FUTILE**  
**not a work cycle,**  
**not an engine**

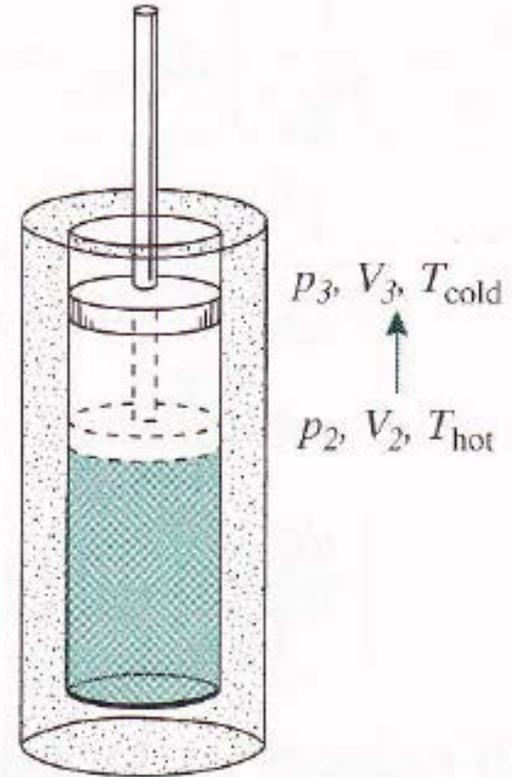
**How to return to starting point**  
**without so much work back in?**

I. Isothermal reversible expansion

$q_1$  is positive  
 $w_1$  is negative



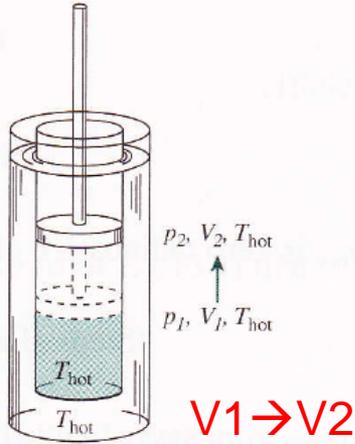
I. Isothermal reversible expansion  
 $q_1$  is positive  
 $w_1$  is negative



II. Adiabatic reversible expansion  
 $q_2 = 0$   
 $w_2$  is negative

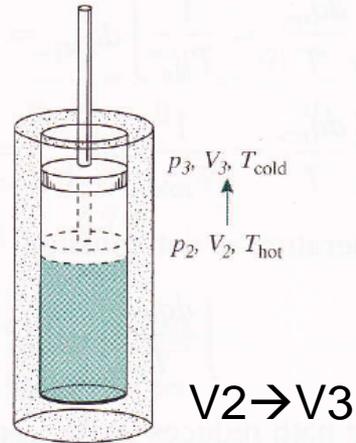
**FIGURE 3.2** A sketch of the four steps of the Carnot-cycle heat engine. The engine is in thermal contact with a hot heat reservoir at  $T_{\text{hot}}$  (step I), a cold heat reservoir at  $T_{\text{cold}}$  (step III), or is thermally isolated (steps II and IV). Steps I and II are expansions in which work is done by the engine. Steps III and IV are compressions in which work is done on the engine.

**HOT**  
**isothermal**  
reversible  
expansion



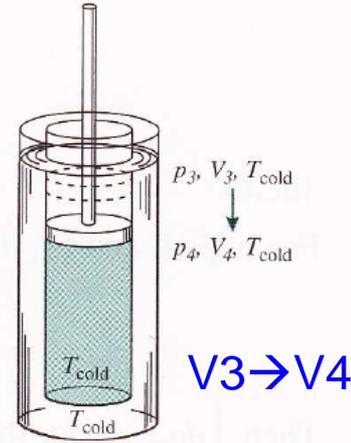
I. Isothermal reversible expansion  
 $q_1$  is positive  
 $w_1$  is negative

Cool the gas  
**adiabatic**  
reversible  
expansion



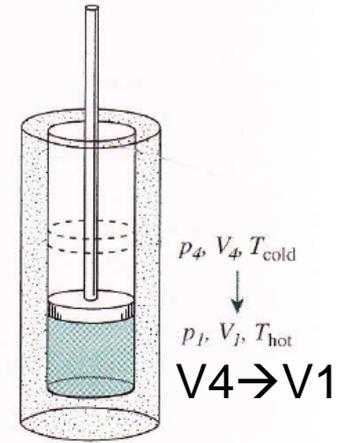
II. Adiabatic reversible expansion  
 $q_2 = 0$   
 $w_2$  is negative

**COLD**  
**isothermal**  
reversible  
compression



III. Isothermal reversible compression  
 $q_3$  is negative  
 $w_3$  is positive

Heat the gas  
**adiabatic**  
reversible  
compression



IV. Adiabatic reversible compression  
 $q_4 = 0$   
 $w_4$  is positive

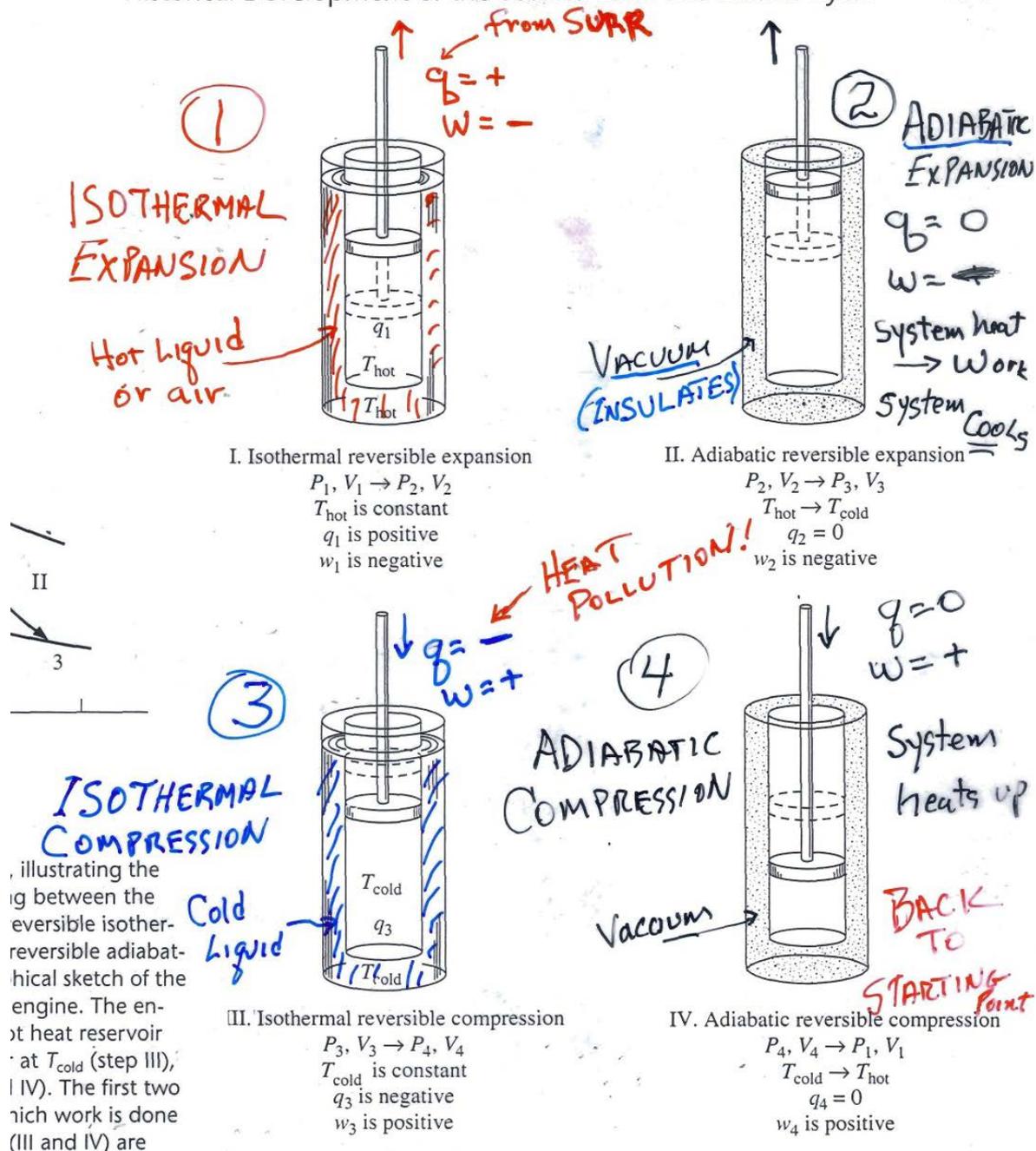
$$w_{rev,hot} = -nRT_{hot} \ln \frac{V_2}{V_1}$$

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

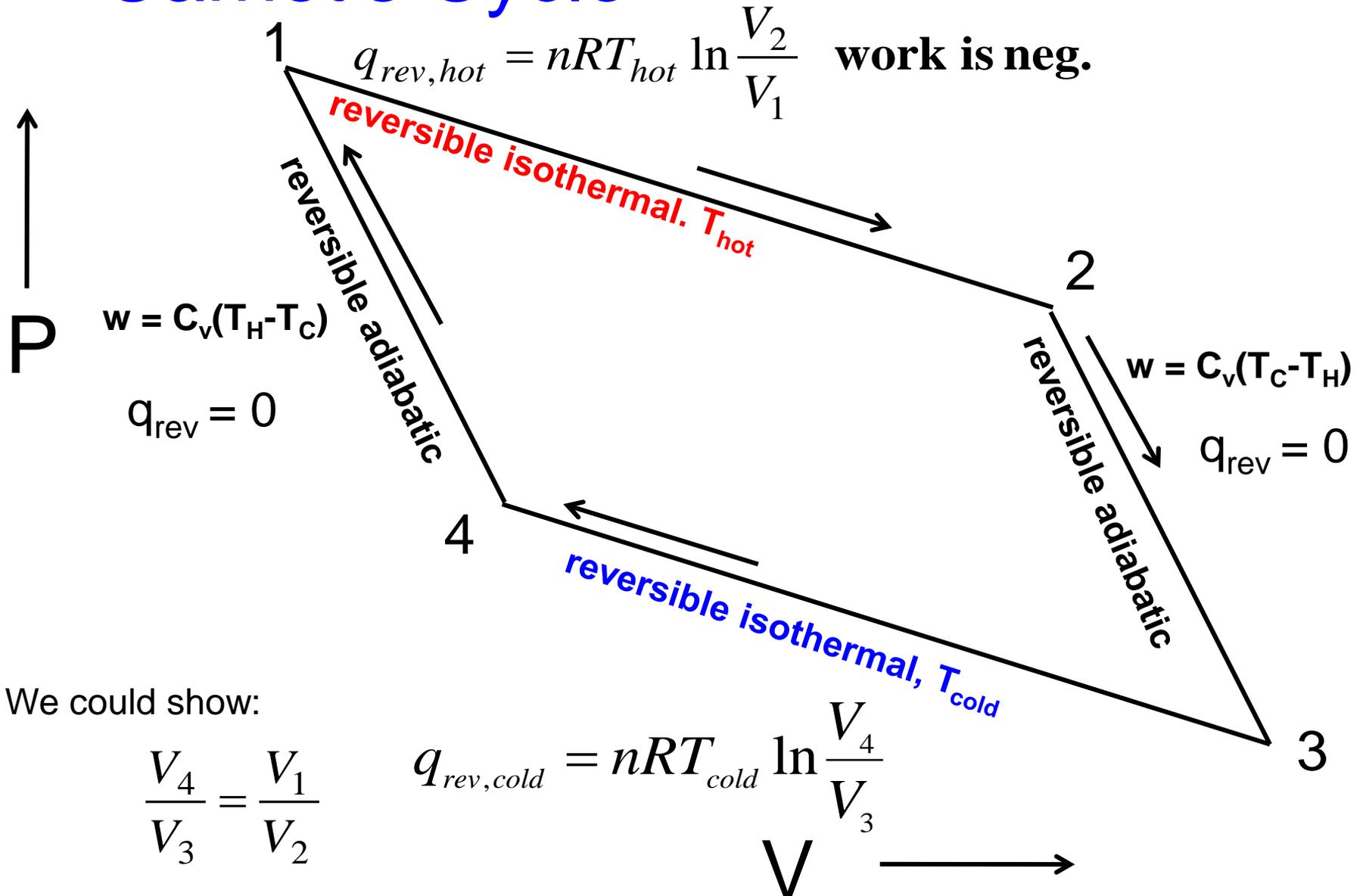
compression at low  $T$  requires less work.

**FIGURE 3.2** A sketch of the four steps of the Carnot-cycle heat engine. The engine is in thermal contact with a hot heat reservoir at  $T_{hot}$  (step I), a cold heat reservoir at  $T_{cold}$  (step III), or is thermally isolated (steps II and IV). Steps I and II are expansions in which work is done by the engine. Steps III and IV are compressions in which work is done on the engine.

Fig. 3.2



# Carnot's Cycle



The two adiabatic parts **cancel**:  $w_{\text{adiabatic}} = \Delta U = C_v (T_{\text{hot}} - T_{\text{cold}})$

$$\frac{\text{Net work out}}{\text{Heat from hot reservoir}} = \frac{nRT_{\text{hot}} \ln \frac{V_2}{V_1} + nRT_{\text{cold}} \ln \frac{V_1}{V_2}}{nRT_{\text{hot}} \ln \frac{V_2}{V_1}}$$

$$= \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$

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

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

$$= 0$$

**Suggesting that  $q_{\text{rev}}/T$  = change in a STATE FUNCTION**

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

$$\oint \frac{dq_{rev}}{T} = 0,$$

and  $dS = \frac{dq_{rev}}{T}$

This proves that **S** is a **STATE FUNCTION**

$$\text{EFFICIENCY} = \frac{T_H - T_C}{T_H}$$

TRUE for ALL Heat engines  
regardless of design & materials

REASON: A MORE EFFICIENT ENGINE COULD  
DRIVE THE REVERSIBLE ONE IN  
REVERSE, i.e., HEAT WOULD  
SPONTANEOUSLY FLOW FROM  
COLD → HOT !

THIS HAS NEVER BEEN SEEN TO HAPPEN

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".