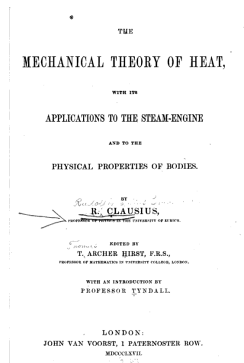


## 02. Entropy and Maxwell's Demon

### I. Clausius' Inequality and Thermodynamic Entropy.

- 1854. "On a modified form of the second fundamental theorem in the mechanical theory of heat".
- 1865. *The Mechanical Theory of Heat*.



- Clausius' "Fundamental Principle" (1854):



"Heat can never pass from a colder to a warmer body *without some other change, connected therewith, occurring at the same time.*"

- Restate as (1865):

"The algebraic sum of all the *transformations* which occur in a cyclical process must always be positive, or in the limit equal to zero."



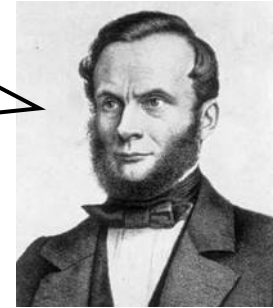
- Formulated in terms of an inequality (Clausius' Inequality):

$$\oint \frac{\delta Q}{T} \leq 0. \quad \delta Q/T = \text{infinitesimal transformation consisting of an element of heat, } \delta Q, \text{ absorbed by the system at temperature } T \text{ (Kelvin scale).}$$

- Note: Clausius distinguishes between heat elements *absorbed* by system,  $\delta Q$ , and heat elements *emitted* by system,  $-\delta Q$ .
- And: His *positive* algebraic sum is meant to apply to *emitted* heat elements.

- For reversible processes, let  $dS = \delta Q_R / T$ . Call  $S$  "entropy":

"... I propose to call the magnitude  $S$  the *entropy* of the body... I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable."



- For a thermally isolated (closed) system, can show that 2nd Law entails:

$$S_{final} - S_{initial} \geq 0.$$

- What this means: For a closed system undergoing an energy transformation, the entropy of the final state cannot be less than the entropy of the initial state.



"... [W]e may express in the following manner the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat:

1. *The energy of the universe is constant.*
2. *The entropy of the universe tends to a maximum.*"

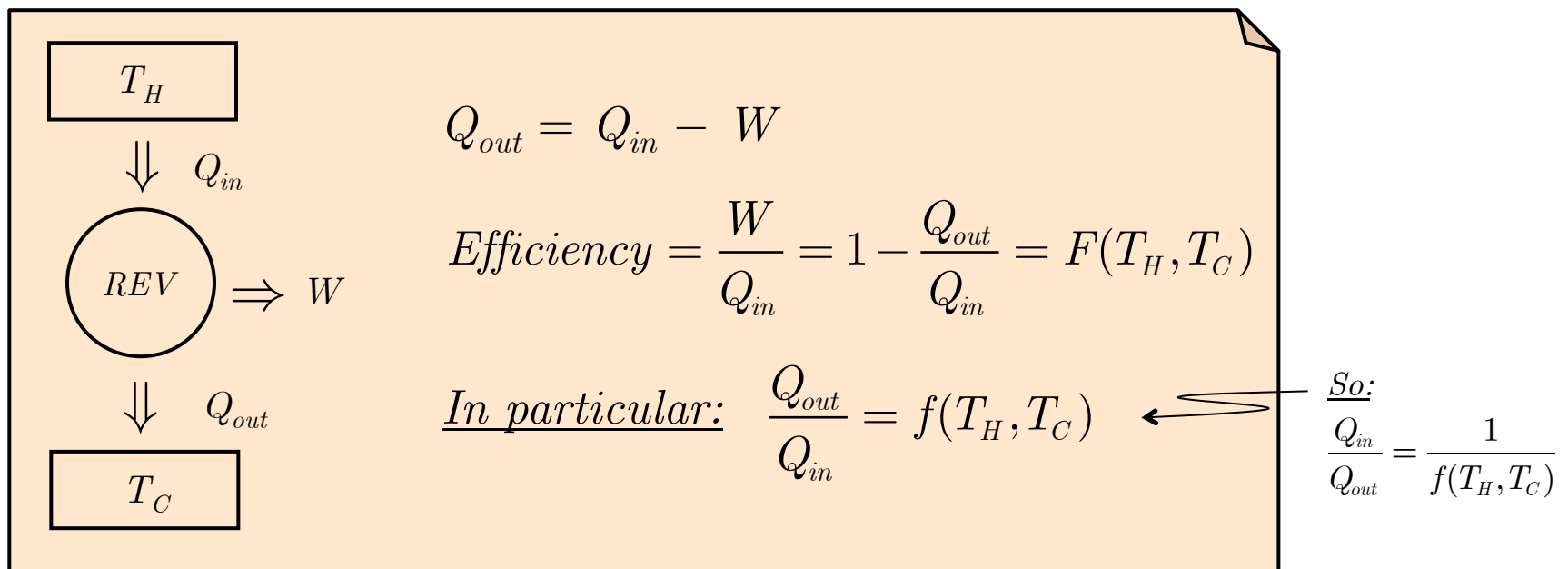
# 1. Derivation of Clausius' inequality $\oint \frac{\delta Q}{T} \leq 0$ .

- First: Let's derive the important relation for reversible heat engines

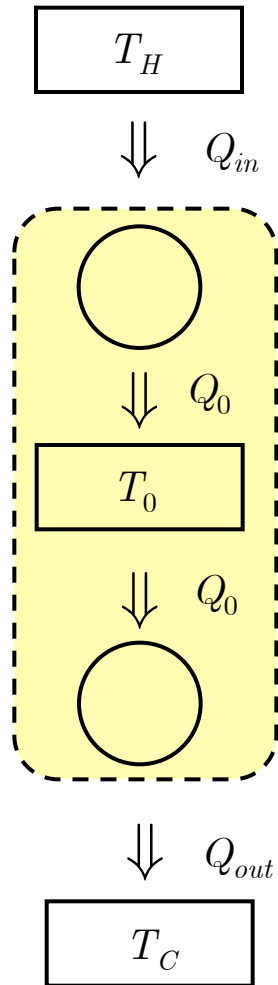
$$\frac{Q_{out}}{Q_{in}} = \frac{T_C}{T_H}$$

where the temperature is measured by the absolute Kelvin scale.

- Recall (Carnot's Claim #2): The efficiency of a reversible heat engine is a function *only* of the temperatures of the hot and cold places.



- Consider a multi-stage *reversible* heat engine:



- Note:  $\frac{Q_{out}}{Q_{in}} = \frac{Q_{out}}{Q_0} \frac{Q_0}{Q_{in}}$

- So:  $\frac{Q_{out}}{Q_{in}} = f(T_C, T_H) = \frac{f(T_C, T_0)}{f(T_H, T_0)} = \frac{f(T_C)}{f(T_H)}$

- Now choose:  $f(T_C) = T_C$ ,  $f(T_H) = T_H$  ← Thomson's (1848) "absolute" temp scale.

- For this "Kelvin" temp scale, and for reversible heat engines:

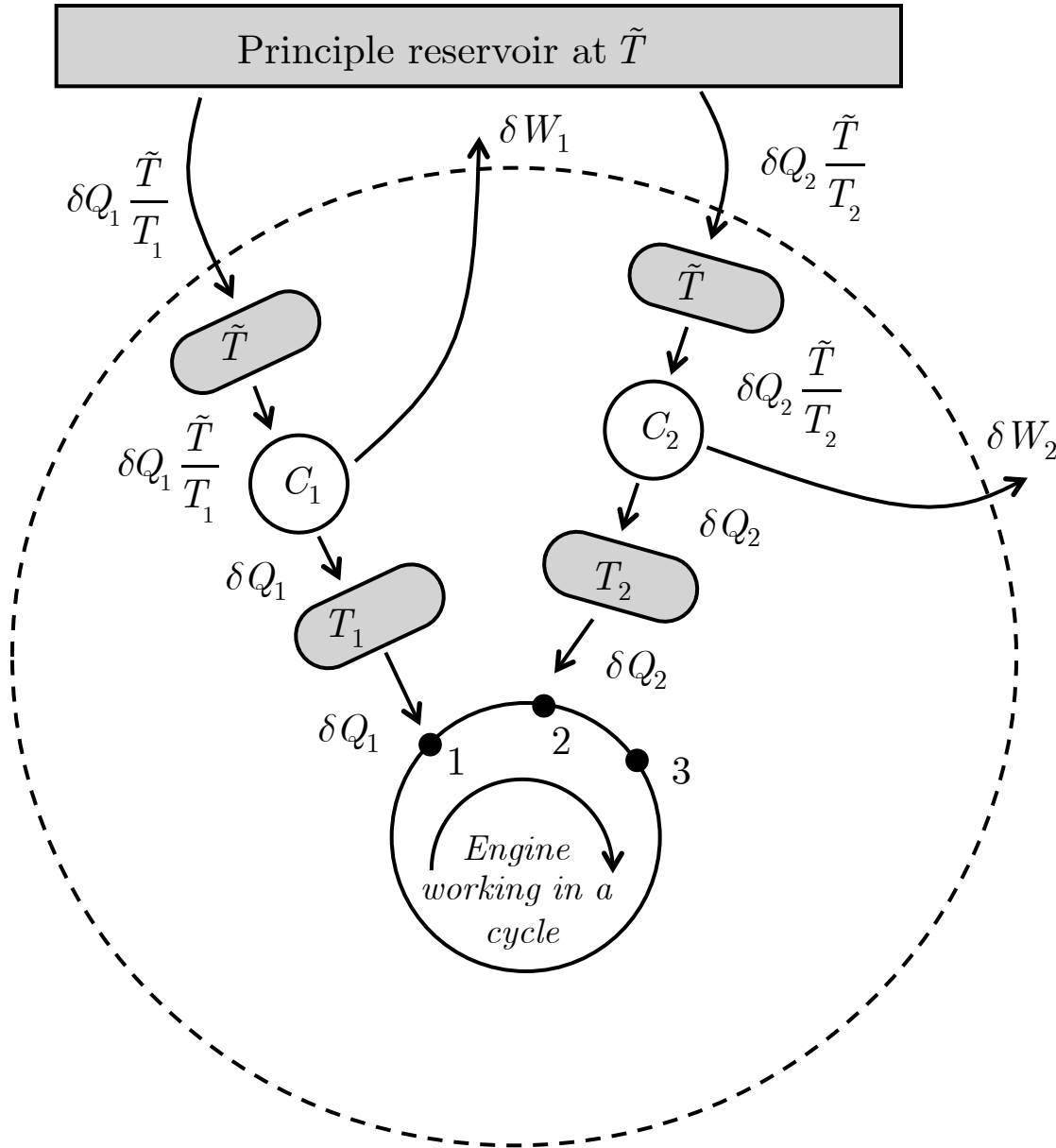
$$\frac{Q_{out}}{Q_{in}} = \frac{T_C}{T_H}$$

or

$$Q_{in} = Q_{out} \frac{T_H}{T_C}$$

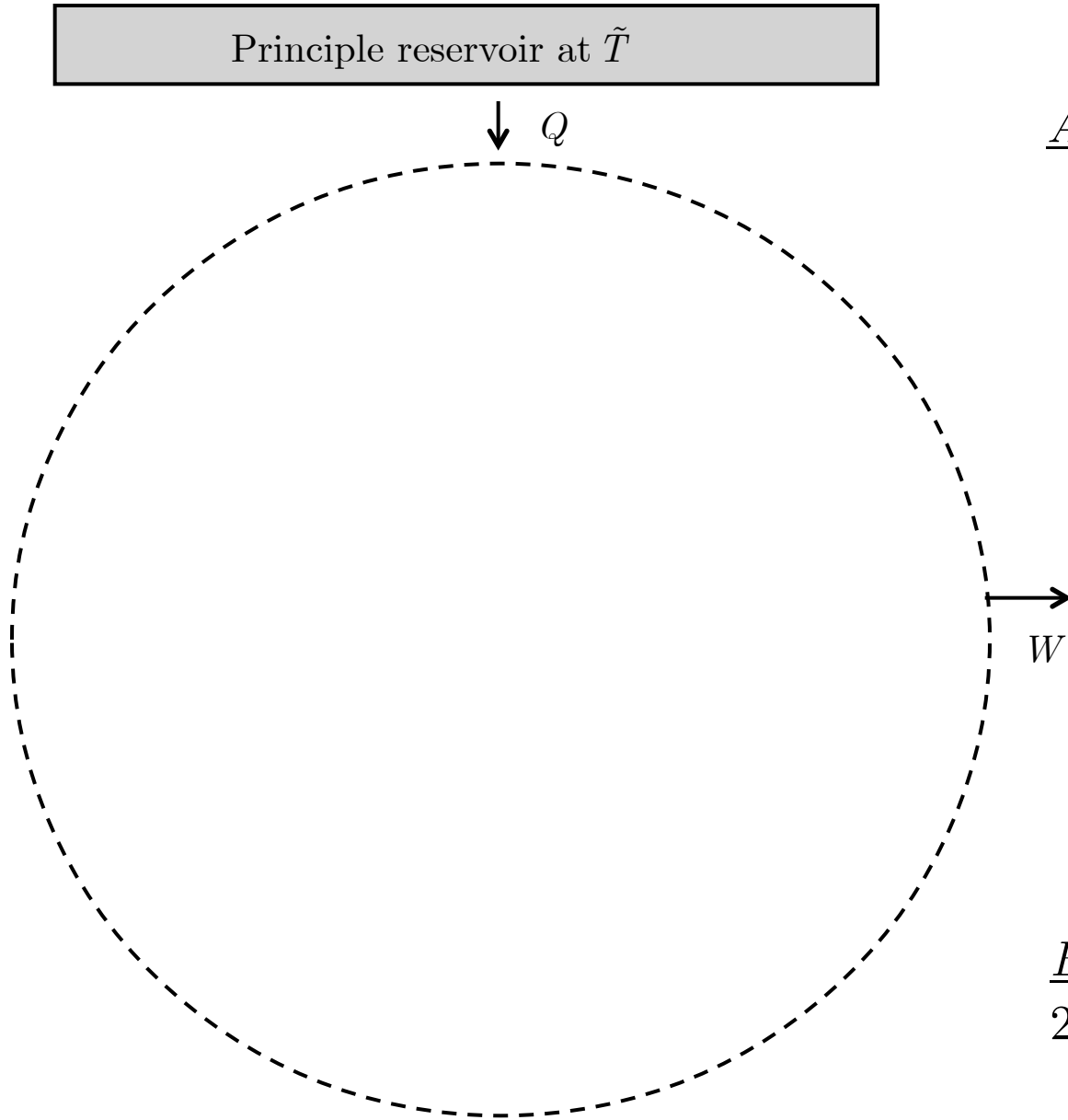
- Now: Consider the following engine working in a cycle in which the initial and final states are identical.

$$Q_{in} = Q_{out} \frac{T_H}{T_C}$$



- Use reservoir at  $T_1$  to inject heat  $\delta Q_1$  to initial state 1.
- Resupply  $T_1$  using reversible heat engine  $C_1$ , which takes heat  $\delta Q_1(\tilde{T}/T_1)$  from reservoir at  $\tilde{T}$ , and performs work  $\delta W_1$ .
- Resupply reservoir at  $\tilde{T}$  with heat  $\delta Q_2(\tilde{T}/T_2)$  from principle reservoir.
- Repeat process.

- Now: Consider the following engine working in a cycle in which the initial and final states are identical.



After complete cycle:

- Total heat supplied is

$$Q = \sum_i \delta Q_i \frac{\tilde{T}}{T_i}$$

- Total work output is

$$W = \sum_i \delta W_i$$

- $\Delta U = U_f - U_i = 0$  (for a cycle)
- So:  $Q = W$

But! This is a violation of the 2nd Law (Thomson version)!

- So:

- Either  $W$  and  $Q$  must be negative: work is done *to* the system and heat is extracted *from* it.
- Or  $W$  and  $Q$  must be zero.

- Thus:  $W = Q \leq 0$ , or  $\tilde{T} \sum_i \frac{\delta Q_i}{T_i} \leq 0$ , or  $\sum_i \frac{\delta Q_i}{T_i} \leq 0$ .

- Hence:  $\oint \frac{\delta Q}{T} \leq 0$ . **Clausius' Inequality**

- What if the cycle is reversible?

- Then:  $-\oint \frac{\delta Q}{T} \leq 0$  or  $\oint \frac{\delta Q}{T} \geq 0$ .

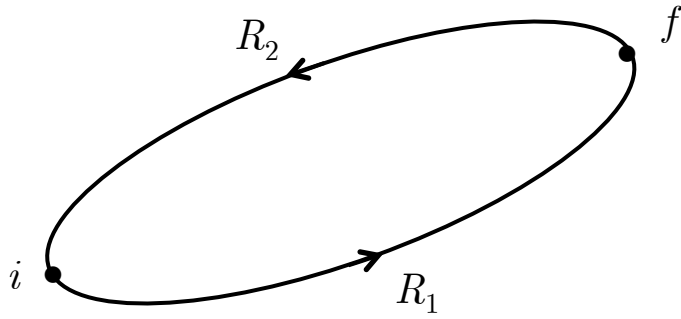
- So:  $W = Q \geq 0$ , or  $\sum_i \frac{\delta Q_i}{T_i} \geq 0$ .

- Hence: In order to be consistent with the first result,

$$\oint_R \frac{\delta Q_R}{T} = 0.$$

## 2. Thermodynamic Entropy $dS = \delta Q_R / T$ .

- Consider a *reversible* cycle:



- Start in initial state  $i$ .
- Take reversible path  $R_1$  to final state  $f$ .
- Return to initial state *via* reversible path  $R_2$ .

- Clausius' inequality is  $\oint_R \frac{\delta Q_R}{T} = \int_{R_1}^f \frac{\delta Q_R}{T} + \int_{R_2}^i \frac{\delta Q_R}{T} = 0$ .

- Thus:  $\int_{R_1}^f \frac{\delta Q_R}{T} = - \int_{R_2}^i \frac{\delta Q_R}{T} = \int_{R_2}^f \frac{\delta Q_R}{T}$

- So:  $\int_R^f \frac{\delta Q_R}{T}$  is *path-independent!*

- Which means: It can be represented by a function, call it  $S$  ("entropy"):

$$\Delta S \equiv S_f - S_i := \int_R^f \frac{\delta Q_R}{T}$$



The *thermodynamic entropy*  $S(f)$  of a state  $f$  is the ratio of the change in heat to temperature of a *reversible* process that connects an initial state  $i$  to  $f$ .

$$\Delta S \equiv S_f - S_i := \int_i^f \frac{\delta Q_R}{T}$$

Characteristics of thermodynamic entropy:

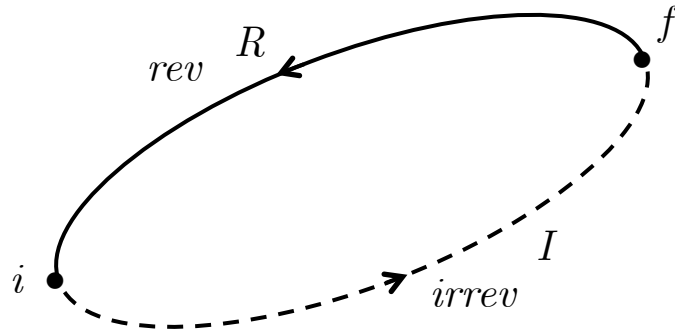
- (1) Only defined for *reversible processes*; *i.e.*, processes that are "quasi-static".
  - *Quasi-static process* = succession of equilibrium states.
  - *Equilibrium state* = state of system in which macroscopic properties (*i.e.*, temperature, volume, pressure, *etc*) are (approximately) constant.
  
- (2) Only defined for *equilibrium states*.
  - *No reference to "disorder" or "chaos"*.
  - *No reference to molecules or particles (gas or otherwise)*.
  - *No reference to "information"*.

- $\Delta S = S_f - S_i$  is defined in terms of a *reversible* process that connects  $i$  to  $f$ .
- For an *irreversible* process,  $\Delta S$  can still be calculated if there is, in principle a reversible process that connects  $i$  and  $f$ .

Example: Heating a beaker of water.

### 3. Principle of Increasing Thermodynamic Entropy

- Consider an irreversible cycle:



- Irreversible cycle consisting of an irreversible process  $I$  from  $i$  to  $f$ , followed by a reversible process  $R$  from  $f$  back to  $i$ .

- Clausius' inequality is  $\int_I^f \frac{\delta Q}{T} + \int_R^i \frac{\delta Q_R}{T} < 0$ , or  $\int_I^f \frac{\delta Q}{T} - \int_i^f \frac{\delta Q_R}{T} < 0$ .

- Thus:  $\Delta S = \int_R^f \frac{\delta Q_R}{T} > \int_I^f \frac{\delta Q}{T}$

Note: If the cycle was *reversible* (i.e., if the path  $I$  was reversible), then the ">" would become an "=".

- So in general:  $\Delta S = \int_R^f \frac{\delta Q_R}{T} \geq \int_i^f \frac{\delta Q}{T}$

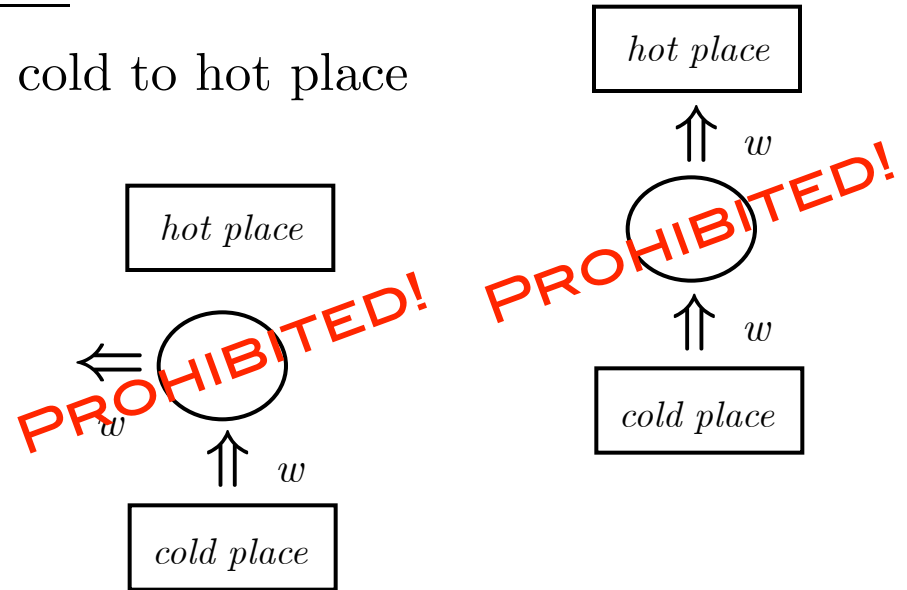
- Now: Suppose the path from  $i$  to  $f$  is *thermally isolated*; i.e.,  $\delta Q = 0$ .

- Then:  $\Delta S \geq 0$  or  $S_f \geq S_i$

- In words: The entropy of a thermally isolated irreversible process increases, and is unaltered in a thermally isolated reversible process.

## 4. Summary of 2nd Law of Thermodynamics

- (1) Clausius Form: No heat transfer from cold to hot place without work input:
- (2) Thomson Form: No conversion of heat to work without exhaust:

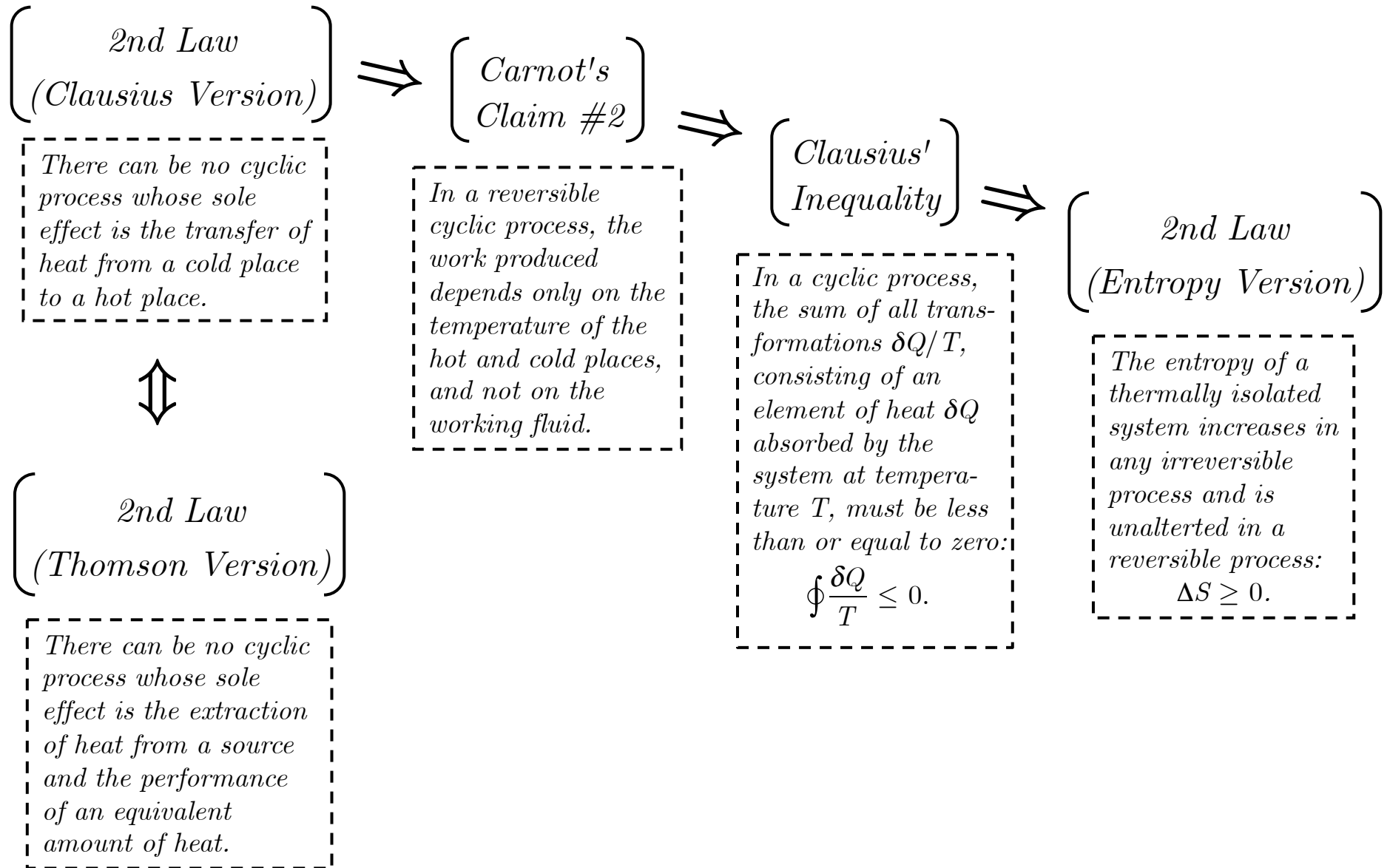


### Consequence of 2nd Law:

The *thermodynamic entropy* of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process.

- These are *absolute* statements.
- They are meant to hold for *all* systems subject to thermodynamical analysis.

• Summary of Entailments:



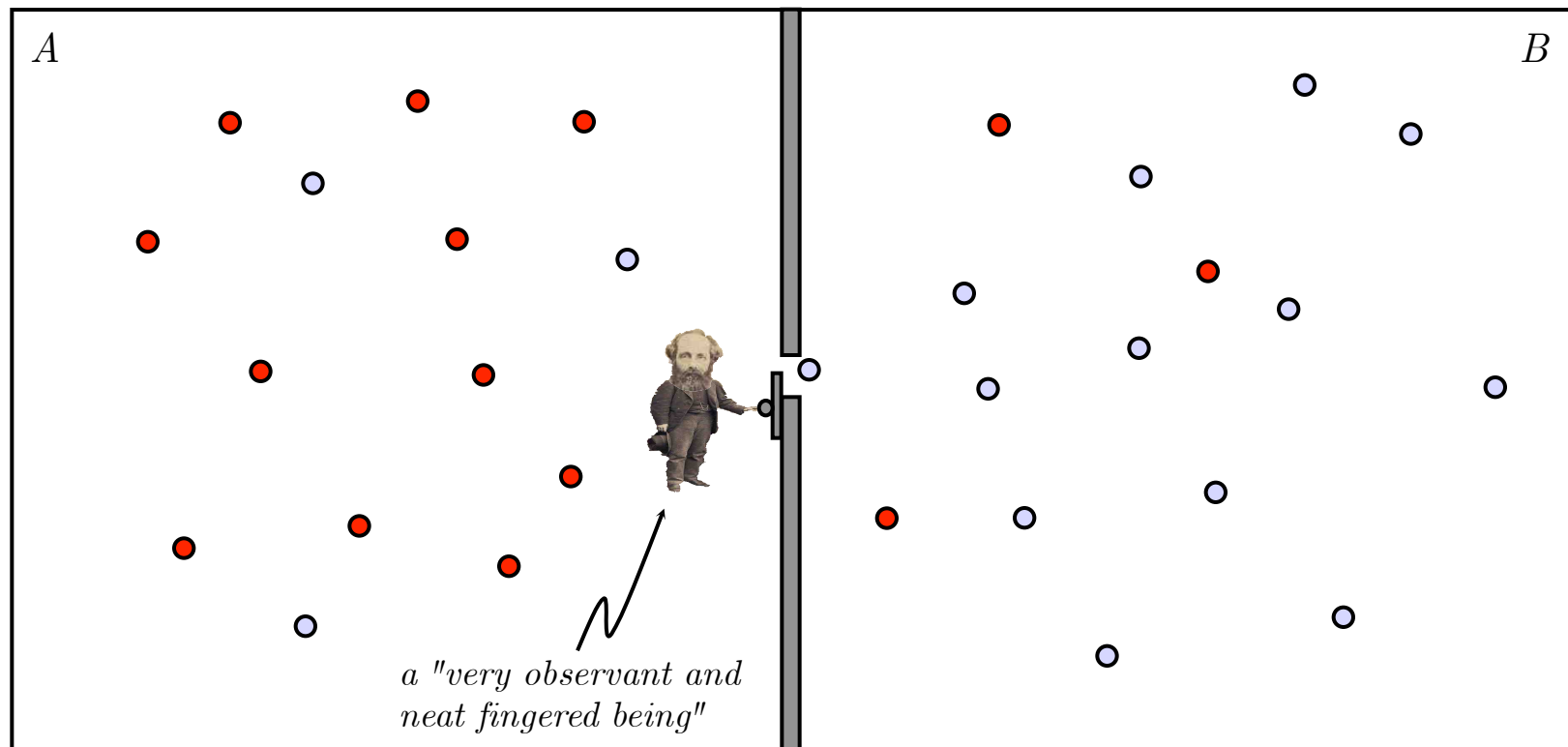
## II. Maxwell's Demon.

### 1. Maxwell's (1867) letter to Tait.

- Consider 2nd Law in the form: "If two things are in contact, the hotter cannot take heat from the colder without external agency."
- Maxwell's counterexample:



*James Clerk  
Maxwell*



- The neat-fingered being only lets hot molecules through to *A* and cold molecules through to *B*.

- Upshot:

"The hot system has got hotter and the cold colder and yet no work has been done, only the intelligence of a very observant and neat fingered being has been employed."



- Moral #1:



"The 2nd Law of Thermodynamics has only statistical certainty."

- In other words: It's very probable, but *not* completely certain, that "If two things are in contact, the hotter cannot take heat from the colder without external agency."

- Moral #2: Attempts to derive the 2nd Law from (deterministic) mechanics will fail.

"...it is rare sport to see those learned Germans contending for the priority of the discovery that the 2nd law of [thermodynamics] is the Hamiltonische Princip... [It] soars along in a region unvexed by statistical considerations while the German Icarus flap their waxen wings in *nephelo coccygia* amid those cloudy forms which the ignorance and finitude of human science have invested with the incommunicable attributes of the invisible Queen of heaven."





- Moral #3: The distinction between dissipated energy (heat that we cannot make use of) and energy available for work depends on our state of knowledge.



[If we supposed]... our senses sharpened to such a degree that we could trace the motions of molecules as easily as we now trace those of large bodies... the distinction between work and heat would vanish...

[The truth of the 2nd Law depends]... on the fact that the bodies we deal with consist of millions of molecules and that we can never get hold of a single molecule."

- In other words: If we were neat-fingered beings capable of knowing the positions and velocities of molecules, the 2nd Law would not apply.

## 2. Vexing Unanswered Questions:

(1) *Why* is the 2nd Law only statistical?

- Are the probabilities really *epistemic*? Do they really reflect our lack of knowledge of the micro-physics (Moral #3)?
  - But then why do the vast majority of observable *macroscopic* systems obey the 2nd Law?
- Are the probabilities *ontic*? Do they reflect an intrinsic probabilistic nature of micro-physical objects?
- Subsequent development of statistical mechanics and attempts to derive 2nd Law within it.

(2) Should the Demon itself be subject to thermodynamics?

- Must be: Otherwise why would we care if a non-thermodynamic demon was capable of violating the 2nd Law of thermodynamics?
- But: If so, then shouldn't we "naturalize" the Demon?

- Perhaps a comprehensive thermodynamical analysis of Demon-plus-system will indicate that the 2nd Law is not violated.
- Subsequent 20th-century history of the Demon:
  - *Fluctuation phenomena as naturalized demons.*
  - *Information-theoretic analyses of entropy.*

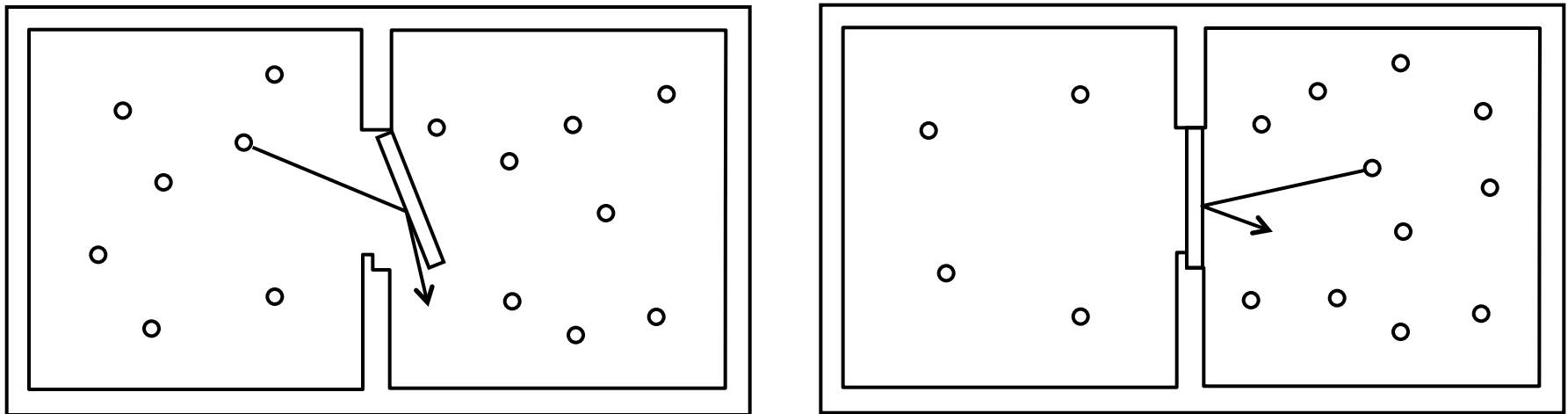
(3) Is Demonology Necessary?

- To investigate the conceptual significance of the 2nd Law, look to securing the foundations of statistical mechanics, as opposed to demon-bashing (Earman & Norton 1998).

### 3. Fluctuation Phenomena and Naturalized Demons

- Early 20th century thermal fluctuation phenomena:
    - *Brownian motion.*
    - *Density fluctuations in fluids near critical states.*
- } Key characteristic:  
*Completely random processes!*
- Idea: Exploit such phenomena to construct devices that violate 2nd Law.

#### (a) Smoluchowski's (1914) trapdoor device:



- Gas in separate chambers initially at equal pressures and temperatures.
- Spring-loaded trapdoor allows *randomly fluctuating* molecules to pass from one side to the other, but not *vice-versa*.
- Expected Result: Build-up of pressure on one side that can be exploited to perform work. Violation of 2nd Law!

## Questions:

- (1) Is this an example of a decrease in entropy of a thermally-isolated system?
    - *Yes!*
  - (2) Can this decrease in entropy be used to perform work?
    - *No! Spring must be sufficiently weak, and trapdoor sufficiently light.*
    - *But then trapdoor itself will be subject to thermal fluctuations that will prevent its intended operation.*
- Smoluchowski's response to (1):
    - Weaken the 2nd Law: **In the long run, on average, a thermally isolated system's entropy will increase.**
  - New (old) question: What if the trapdoor is replaced with an intelligent being who knows when to open/close it?

## (b) Szilard on Entropy and Information

(1929) "On the Decrease of Entropy in a Thermodynamical System by the Intervention of Intelligent Beings"

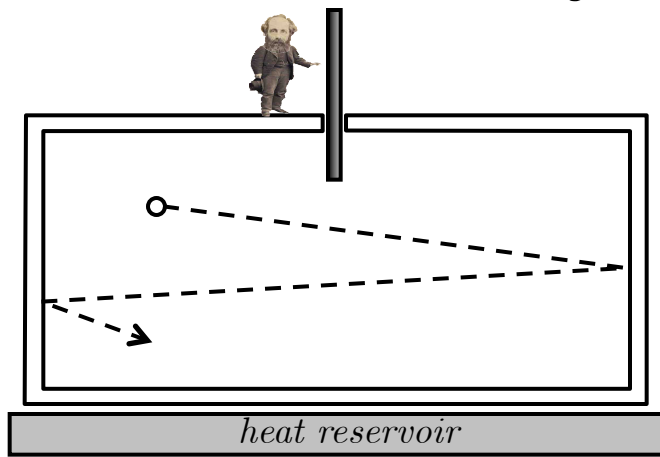
Claim: Any device that employs fluctuations in an attempt to violate the 2nd Law will fail since there is an inevitable hidden entropy cost in the acquisition of information needed to run the device.

"...measurements themselves are necessarily accompanied by a production of entropy."

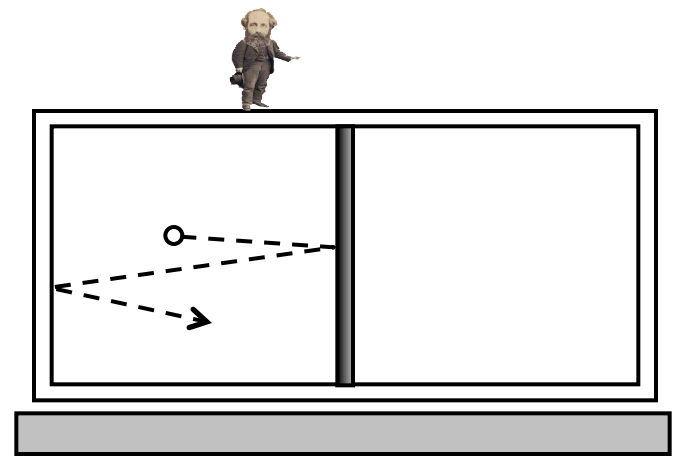
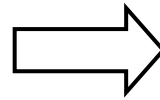


*Leo Szilard*

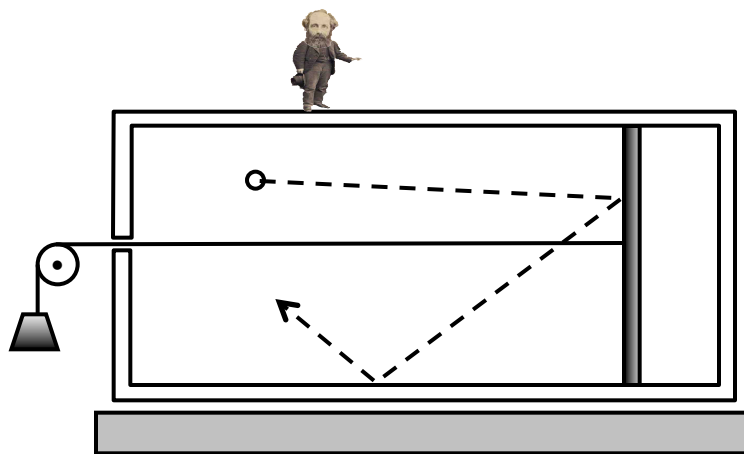
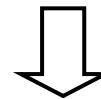
# *Szilard's One-Molecule Engine*



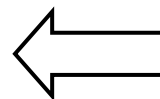
(a) Single molecule exhibiting thermal fluctuations. System at const. temp.



(b) Being inserts partition/piston *and determines which side molecule is on.*



(c) Being attaches weight to side with molecule. Gas expands reversibly and isothermally by absorbing heat from reservoir. Work performed on weight.



(d) Weight is detached. Partition/piston removed. Cycle returns to (a).

- Result: Violation of 2nd Law! Heat converted to work with no exhaust.

- In particular:

$$Q = W = \int_{V_i}^{V_f} P dV$$

$$= \int_{V_i}^{V_f} \frac{kT}{V} dV \quad \leftarrow \text{for an ideal gas}$$

$$= kT \log \frac{V_f}{V_i} = kT \log 2 \quad \leftarrow \begin{array}{l} \text{assuming partition is} \\ \text{inserted down the middle} \\ (V_f = 2V_i) \end{array}$$

○ So: Change in entropy is  $\Delta S = \int_R^f \frac{\delta Q_R}{T} = 0 - \frac{kT \log 2}{T} = \boxed{-k \log 2}$

*A decrease in entropy (in reservoir)!*

Szilard's Solution: There must be an entropy increase of  $k \log 2$  in the being which balances the entropy decrease in the reservoir.



This entropy increase is associated with measurement:

- First: Assume only two possible measurement outcomes (simplest case).
- Let  $\bar{S}_1, \bar{S}_2$  be the entropies associated with outcomes 1 and 2, respectively.

Claim: A lower bound on  $\bar{S}_1, \bar{S}_2$  is given by:

$$e^{-\bar{S}_1/k} + e^{-\bar{S}_2/k} \leq 1$$

Why?

- Let  $w_1, w_2$  be the probabilities of getting outcomes 1 and 2, respectively.
- Then (it turns out), lower bounds for  $\bar{S}_1$  and  $\bar{S}_2$  are given by:

$$\bar{S}_1 \geq -k \log w_1 \quad \bar{S}_2 \geq -k \log w_2$$

or

$$w_1 \geq e^{-\bar{S}_1/k} \quad w_2 \geq e^{-\bar{S}_2/k}$$

- And: The claim then follows from  $w_1 + w_2 = 1$ .

Definition: The average entropy cost of measurement per cycle is

$$\bar{S} = w_1 \bar{S}_1 + w_2 \bar{S}_2$$

- Now show that for any values of  $\bar{S}_1, \bar{S}_2$  that satisfy lower-bound constraint, the resulting value for  $\bar{S}$  is no less than the entropy decrease that violates the 2nd Law.

Ex: Szilard choses  $\bar{S}_1 = \bar{S}_2 = k \log 2$ .

○ These satisfy lower-bound constraint:

$$e^{-\bar{S}_1/k} + e^{-\bar{S}_2/k} = 2e^{-\log 2} \leq 1$$

○ And:  $\bar{S} = w_1 \bar{S}_1 + w_2 \bar{S}_2 = k \log 2$

- Thus: On average, the entropy increase due to measurement is no less than the entropy decrease from the conversion of heat to work.
- So: The 2nd Law is saved.