Chapter 20

The 2nd and 3rd Laws of Thermodynamics

The Second Law of Thermodynamics

The second law of thermodynamics (Clausius Statement): Heat *never* flows spontaneously from a colder body to a hotter body.

Any process that involves dissipation of energy is not reversible.

Any process that involves heat transfer from a hotter object to a colder object is not reversible.

Entropy

Entropy is a state variable and is not a conserved quantity.

Entropy is a measure of a system's disorder.

Heat flows from objects of high temperature to objects at low temperature because this process increases the disorder of the system.

Entropy

If an amount of heat Q flows into a system at constant temperature, then the change in entropy is

$$\Delta S = \frac{Q}{T}.$$

Every irreversible process increases the total entropy of the universe. Reversible processes do not increase the total entropy of the universe.

The Second Law of Thermodynamics

(Entropy Statement)

The entropy of the universe never decreases.

Example:

An ice cube at 0.0 °C is slowly melting.

What is the change in the ice cube's entropy for each 1.00 g of ice that melts?

To melt ice requires $Q = mL_f$ joules of heat. To melt one gram of ice requires 333.7 J of energy.

The entropy change is $$\Delta S = \frac{Q}{T} = \frac{333.7\text{ J}}{273\text{ K}} = 1.22\text{ J/K.}$$

Statistical Interpretation of Entropy

A **microstate** specifies the state of each constituent particle in a thermodynamic system.

A **macrostate** is determined by the values of the thermodynamic state variables.

Table 15.3

Possible Results of Tossing Four Coins

Macrostate	Microstates	Number of Microstates	Probability of Macrostate
4 heads	HHHH	1	$\frac{1}{16}$
3 heads	HHHT HHTH HTHH THHH	4	$\frac{4}{16}$
2 heads	HHTT HTHT HTTH THHT THTH TTHH	6	$\frac{6}{16}$
1 head	HTTT THTT TTHT TTTH	4	$\frac{4}{16}$
0 heads	TTTT	1	$\frac{1}{16}$
	Total number of microstates = 16		

$$\text{probability of a macrostate} = \frac{\text{number of microstates corresponding to the macrostate}}{\text{total number of microstates for all possible macrostates}}$$

The number of microstates for a given macrostate is related to the entropy.

$$S = k \ln \Omega$$

where Ω is the number of microstates.

Example:

For a system composed of two identical dice, let the macrostate be defined as the sum of the numbers showing on the top faces.

What is the maximum entropy of this system in units of Boltzmann's constant?

Example continued:

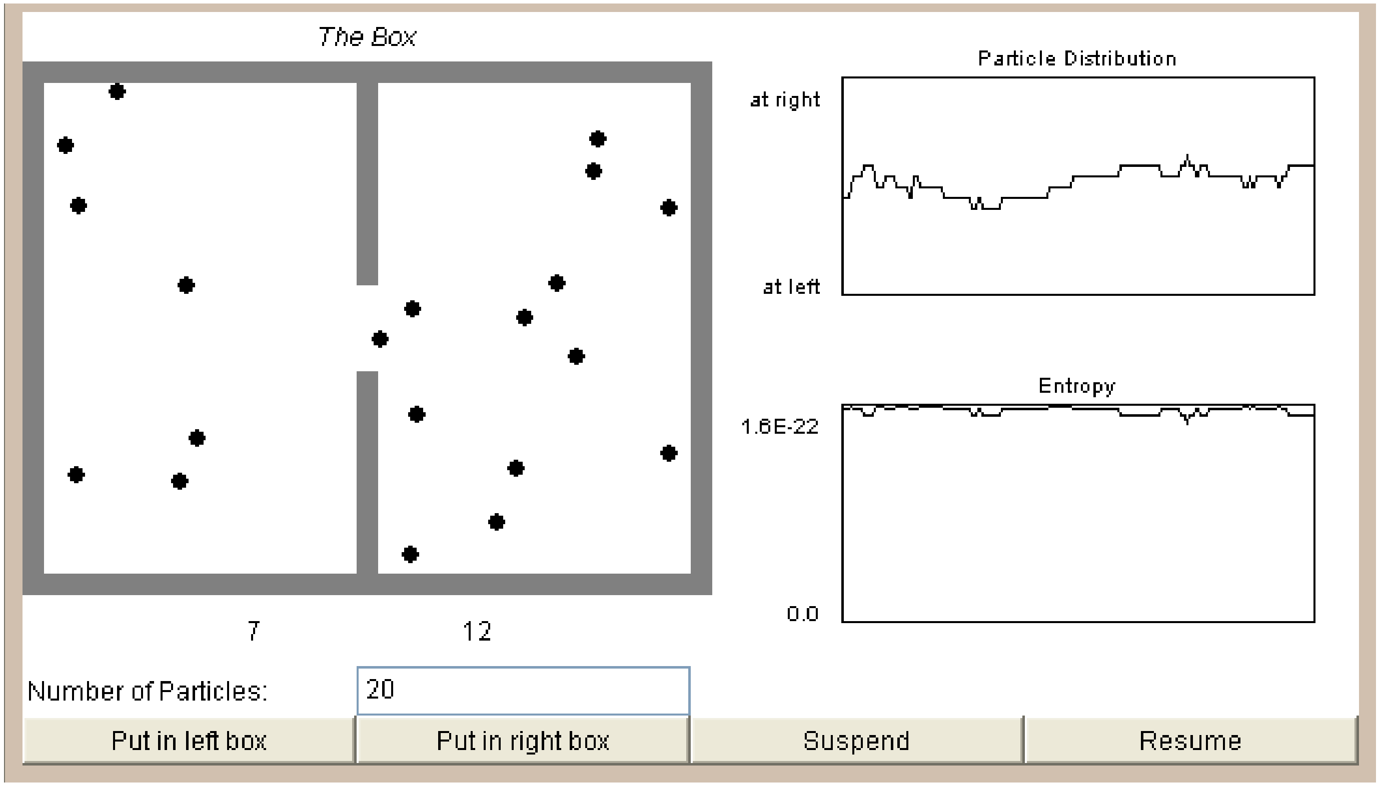
Sum	Possible microstates
2	(1,1)
3	(1,2); (2,1)
4	(1,3); (2,2); (3,1)
5	(1,4); (2,3); (3,2); (4,1)
6	(1,5); (2,4), (3,3); (4,2); (5,1)
7	(1,6); (2,5); (3,4), (4,3); (5,2); (6,1)
8	(2,6); (3,5); (4,4) (5,3); (6,2)
9	(3,6); (4,5); (5,4) (6,3)
10	(4,6); (5,5); (6,4)
11	(5,6); (6,5)
12	(6,6)

Example continued:

The maximum entropy corresponds to a sum of 7 on the dice. For this macrostate, $\Omega = 6$ with an entropy of

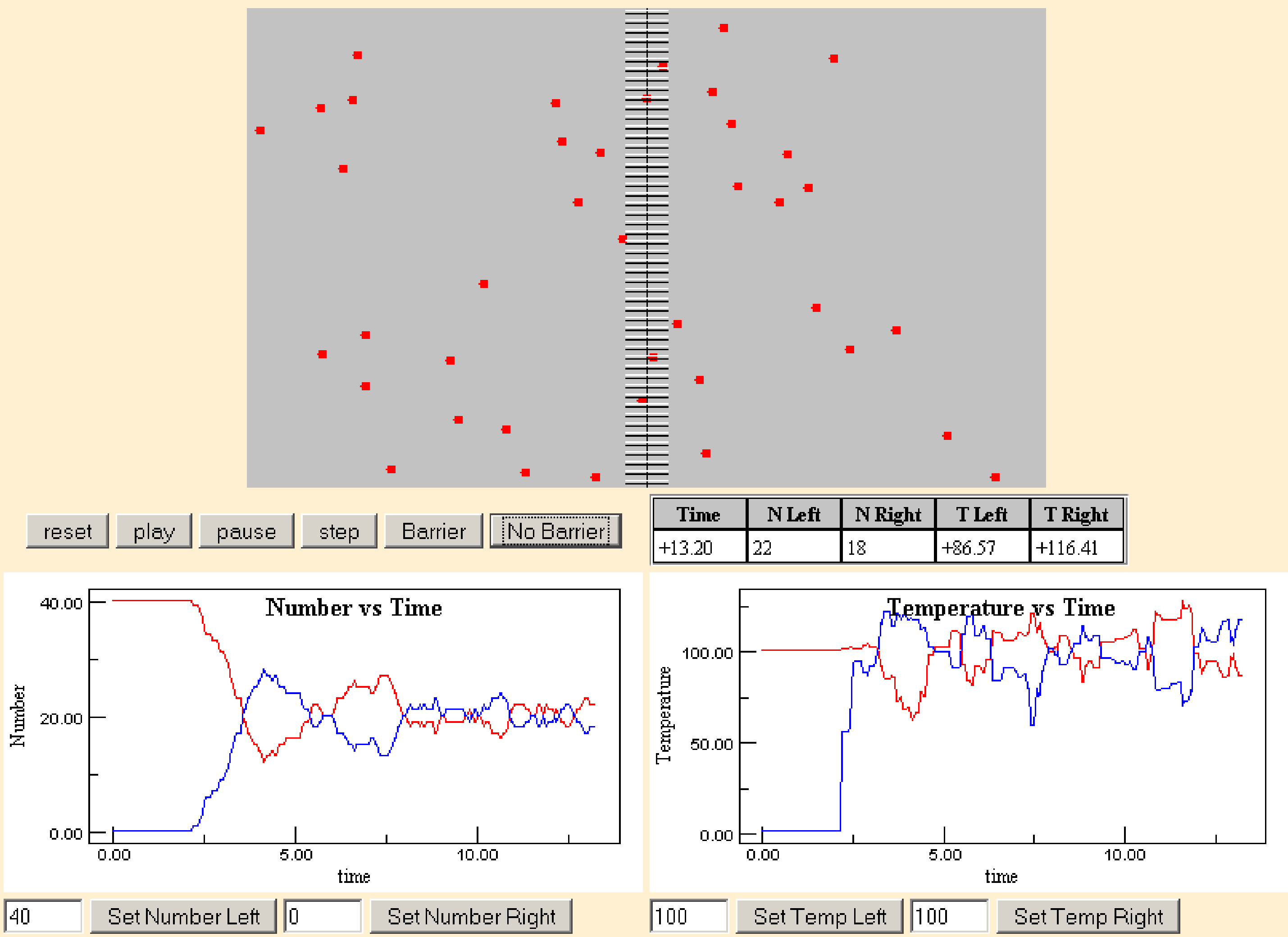
$$S = k\ln\Omega = k\ln 6 = 1.79k.$$

The Disappearing Entropy Simulation



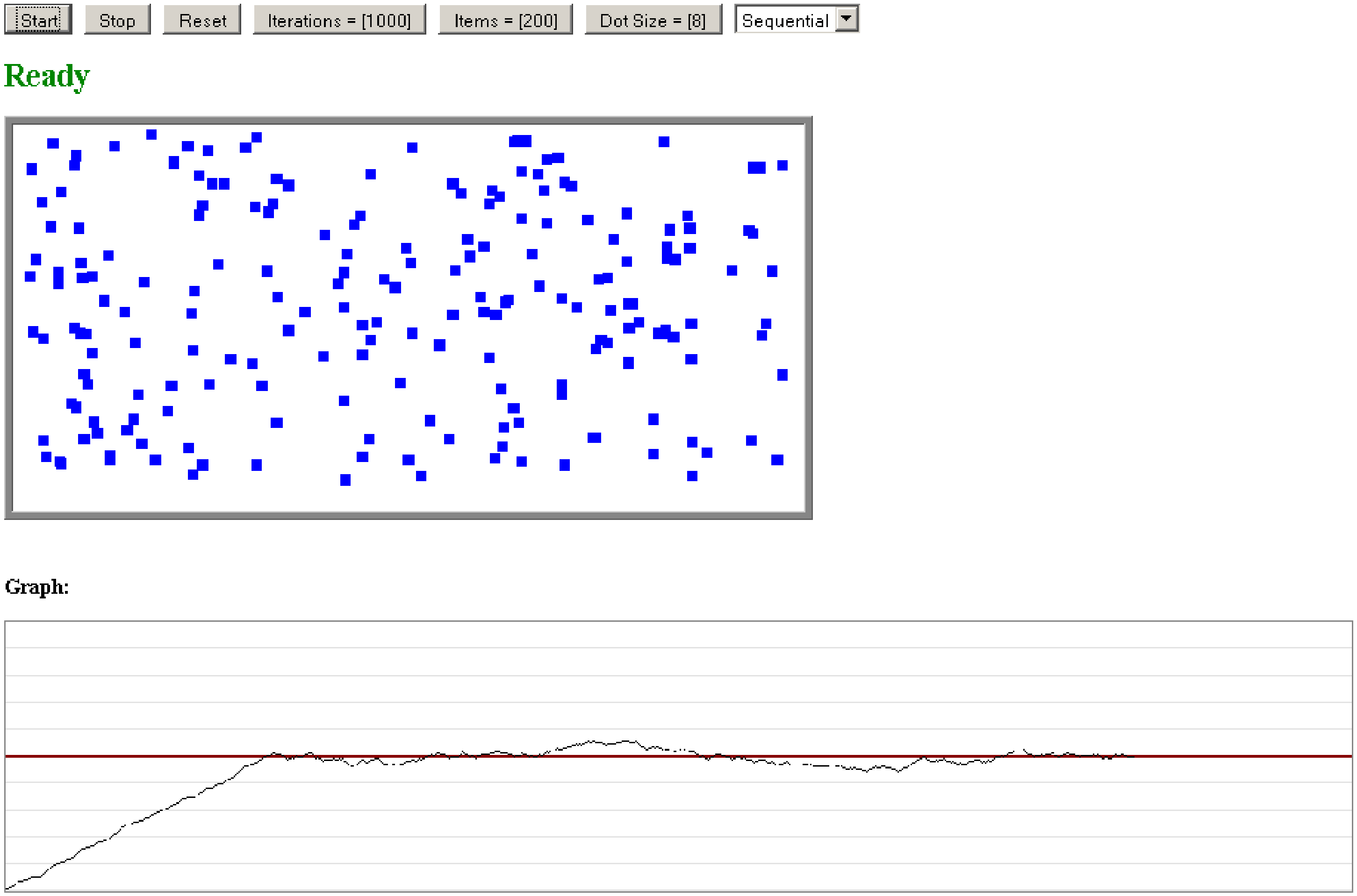
http://mats.gmd.de/~skaley/vpa/entropy/entropy.html

Microscopic Interpretation of Entropy



http://ww2.lafayette.edu/~physics/files/phys133/entropy.html

Gas Expansion - Entropy



http://www.ariehbennaim.com/simulations/index.htm

The number of microstates for a given macrostate is related to the entropy.

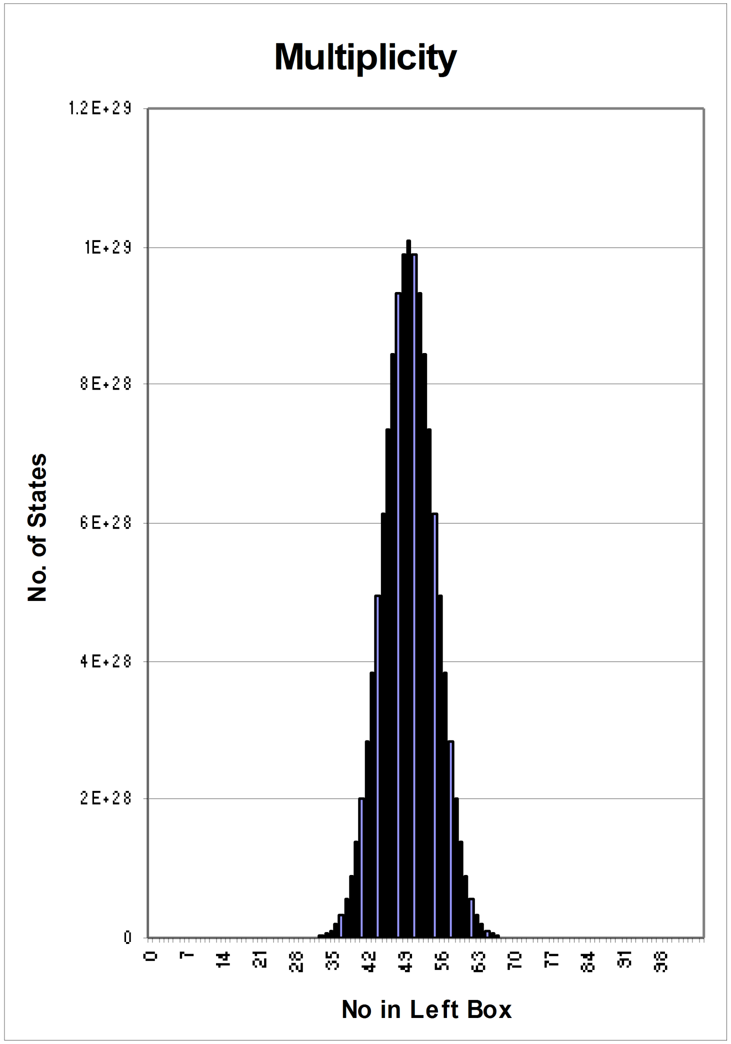
$$S = k \ln \Omega$$

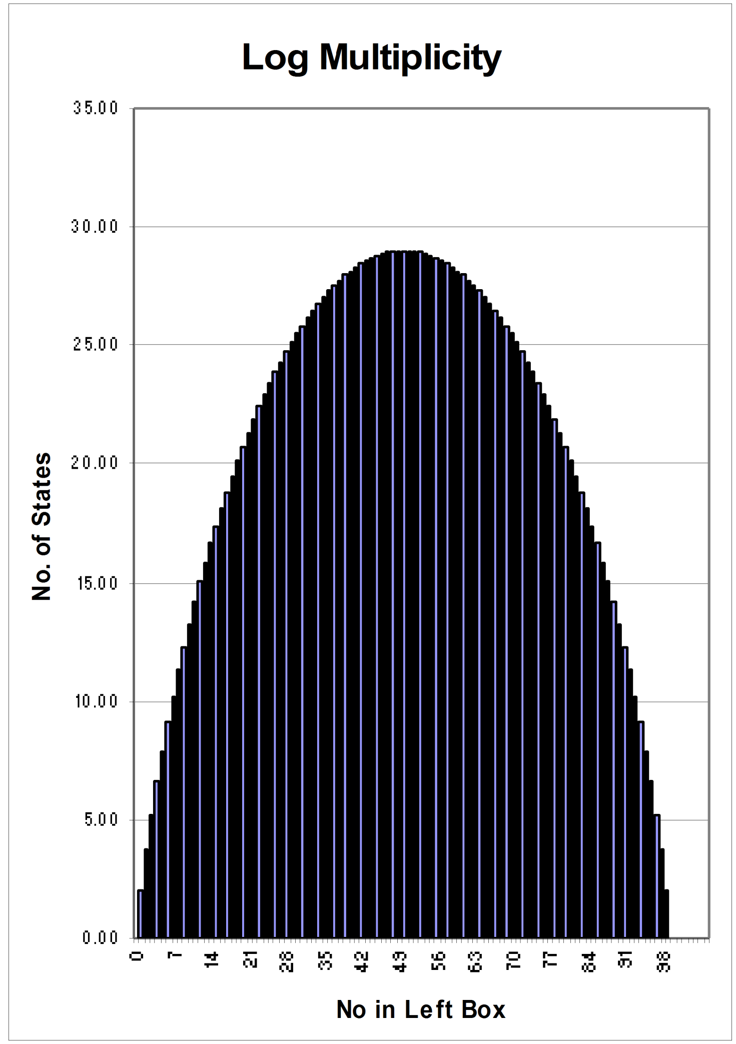
where Ω is the number of microstates.

$$\Omega = (n_1 + n_2)!/(n_1! \times n_2!)$$

n_1 is the number of balls in the box on the left.
n_2 is the number of balls in the box on the right.

Equilibrium is the Most Probable State N=100





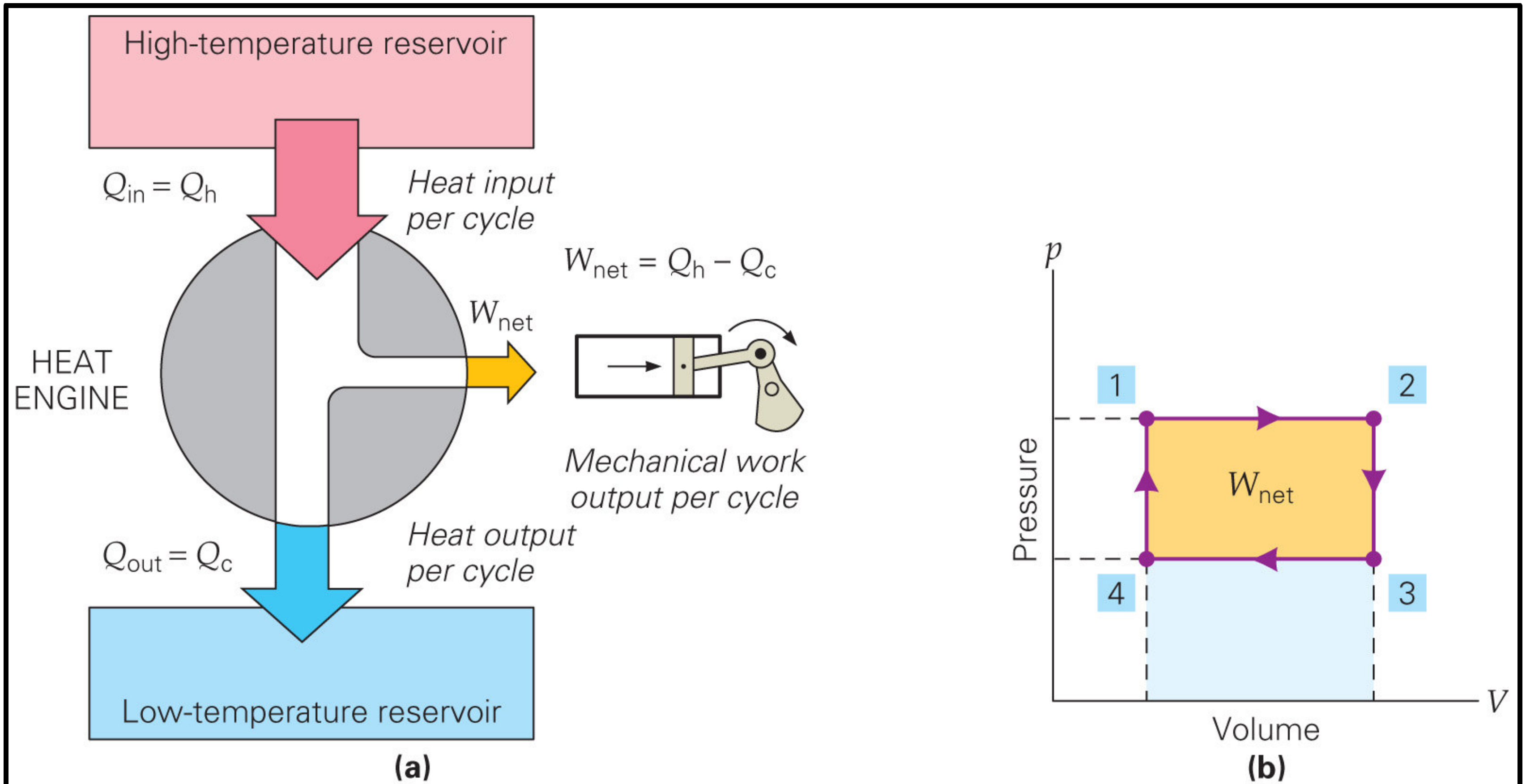
The Third Law of Thermodynamics

The third law of thermodynamics is a statistical law of nature regarding entropy and the impossibility of reaching absolute zero of temperature. The most common enunciation of third law of thermodynamics is:

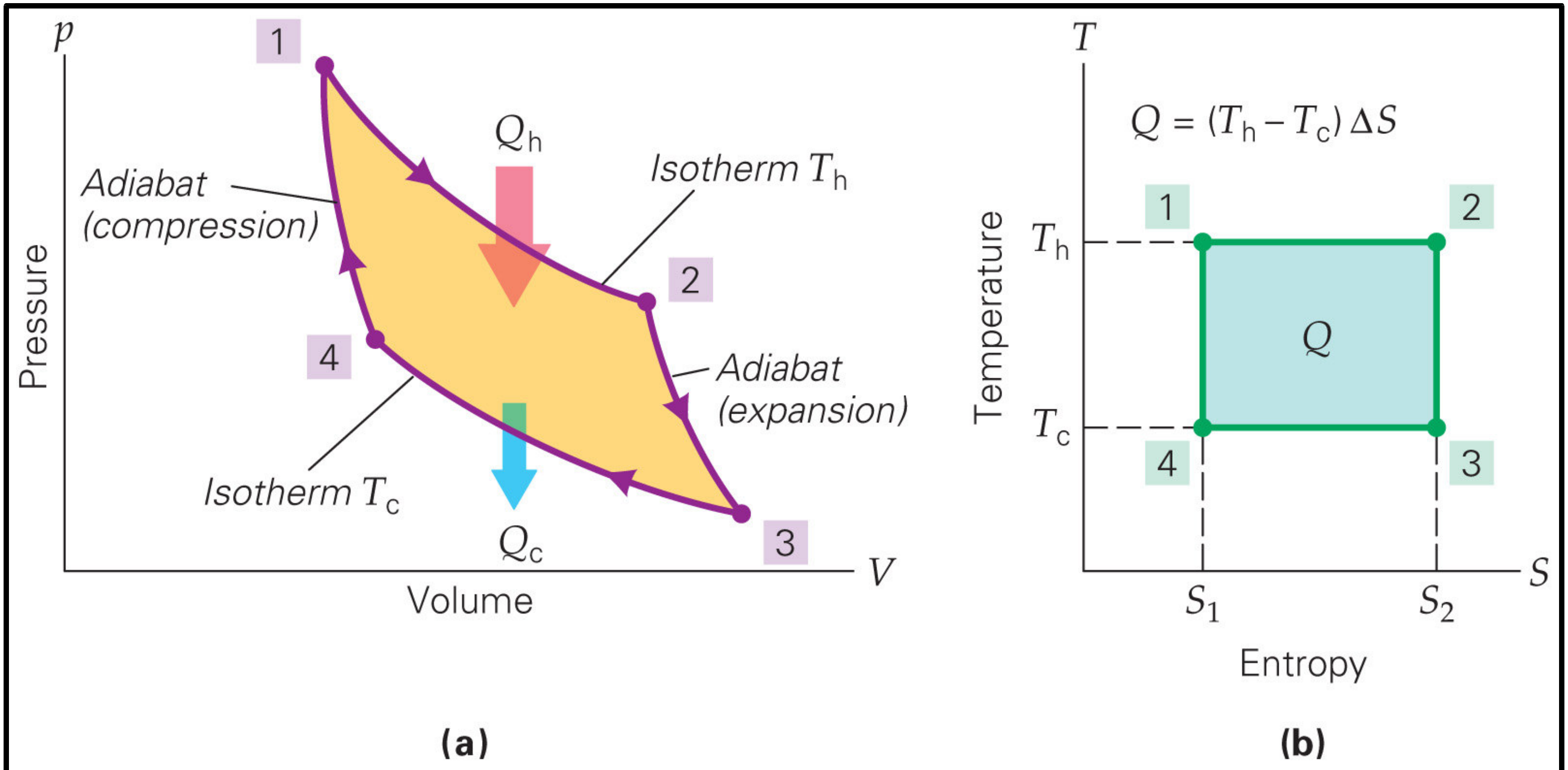
“ As a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.”

It is impossible to cool a system to absolute zero by a process consisting of a finite number of steps.

Heat Engine Operation



Carnot Cycle - Ideal Heat Engine



Carnot Cycle - Ideal Heat Engine

Process efficiency

$$\acute{\eta} = 1 - \frac{T_L}{T_H}$$

No heat engine can run at 100% efficiency. Therefore T_L can never be zero. Hence absolute zero is unattainable.

The British scientist and author C.P. Snow had an excellent way of remembering the three laws:

1. **You cannot win** (that is, you cannot get something for nothing, because matter and energy are conserved).

2. **You cannot break even** (you cannot return to the same energy state, because there is always an increase in disorder; entropy always increases).

3. **You cannot get out of the game** (because absolute zero is unattainable).