

Midterm Exam Problem 10

10. What would be the greatest effect on the ideal gas law if there is a slight attractive force between the molecules?

A) At low densities, the pressure would be less than that predicted by the ideal gas law.

B) At high densities, the pressure would be less than that predicted by the ideal gas law.

C) At high densities, the pressure would be greater than that predicted by the ideal gas law.

D) At low densities, the pressure would be higher than that predicted by the ideal gas law.

E) There is no effect.

Example of using van der Waals equation $P = RT/(V-b) - a/V^2$ for $n = 1$ mole

At $T = 273\text{K}$, applying the ideal gas law to 1 mole of CO_2 in $V = 22.4$ L we get $P = 1$ atm (STP). Using the van der Waals equation, we find $P = 0.995$ atm, so indeed **P is slightly less.**

But the situation reverses at high density, where the $RT/(V-b)$ term becomes more important. For example, if we compress the CO_2 from $V = 22.4$ L to $V = 0.05$ L, the ideal gas law gives $P = 448$ atm while the van der Waals equation gives 1620 atm, so at high density the pressure **P is greater** than that predicted by the ideal gas law.

However, I apologise that problem 10 was ambiguous, and I will be happy to give 5 points credit for answer B as well as A on problem 10 if you turn your Midterm in again by next week's lecture.

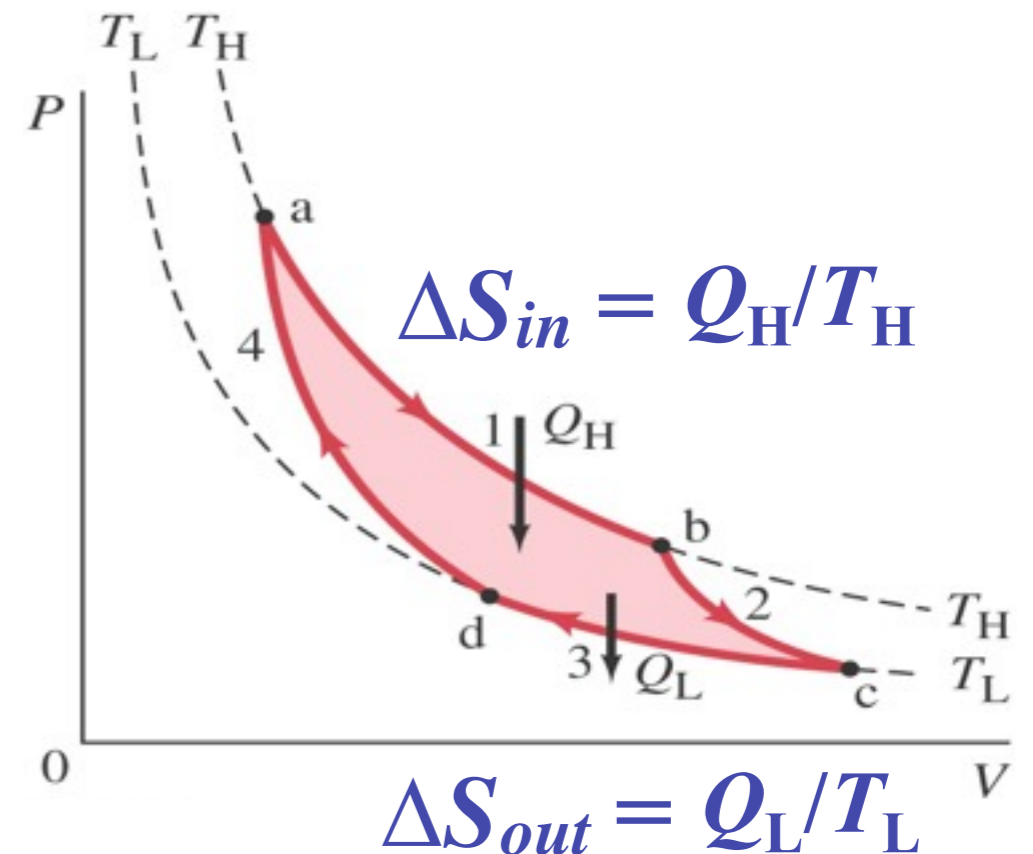
Note: The Final Exam is Wed Dec 11 4 to 7 pm, not 5 to 8 pm as the Syllabus said.

Physics 5D - Lecture 7 - Nov 25, 2013

Understanding Entropy

The Carnot cycle consists of:

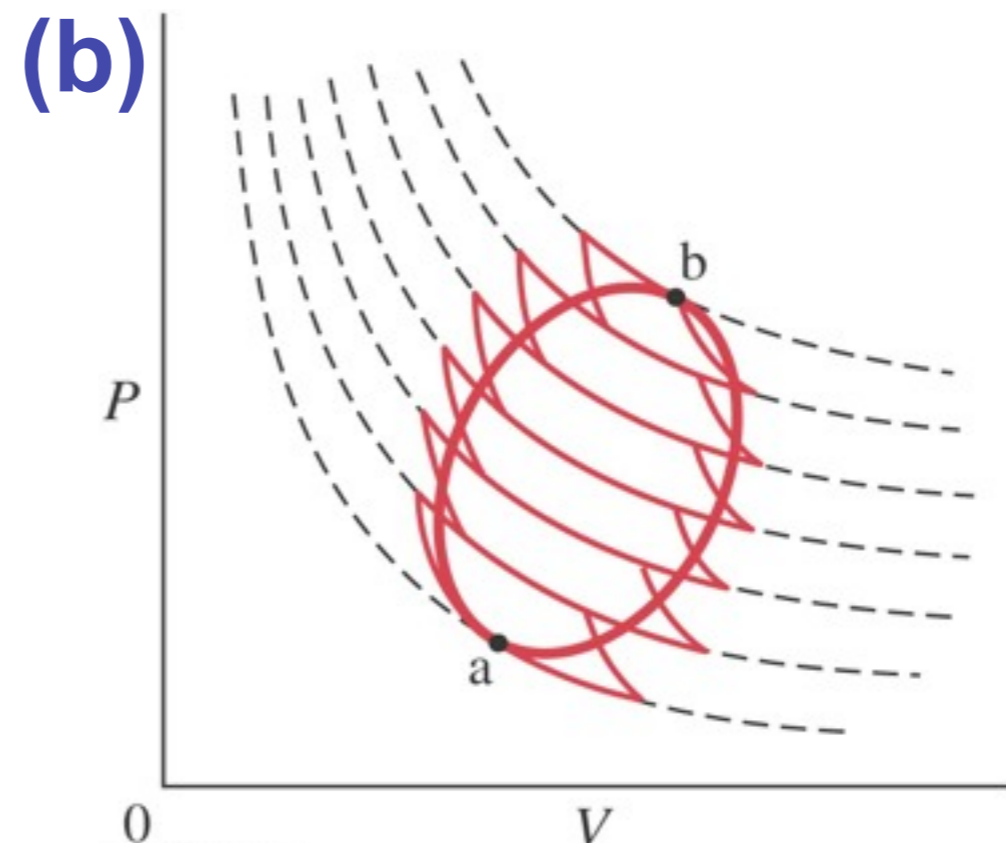
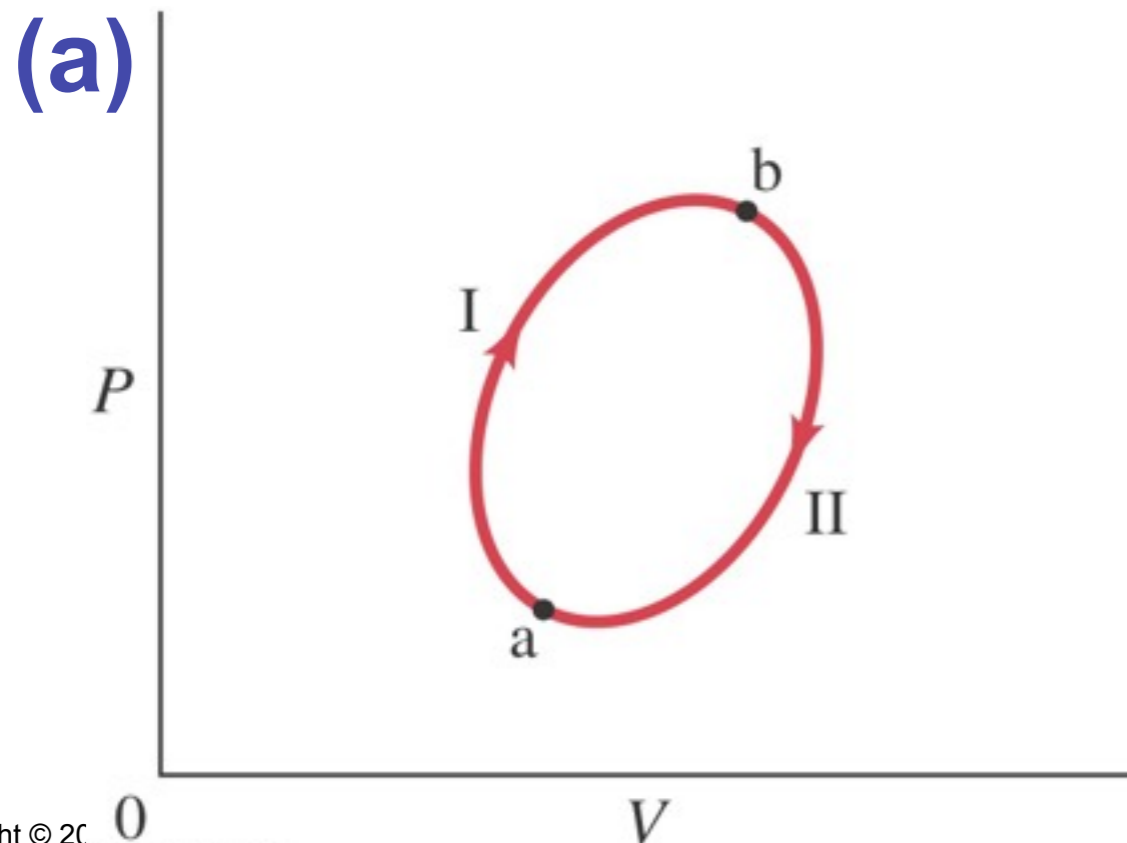
- Isothermal expansion ab
- Adiabatic expansion bc
- Isothermal compression cd
- Adiabatic compression da



The change in entropy S when an amount of heat Q is added in a reversible process at constant T is $\Delta S = Q/T$. For a Carnot cycle, we proved that $Q_H/T_H = Q_L/T_L$, so it follows that $\Delta S = Q_H/T_H - Q_L/T_L = 0$.

Entropy is a State Variable

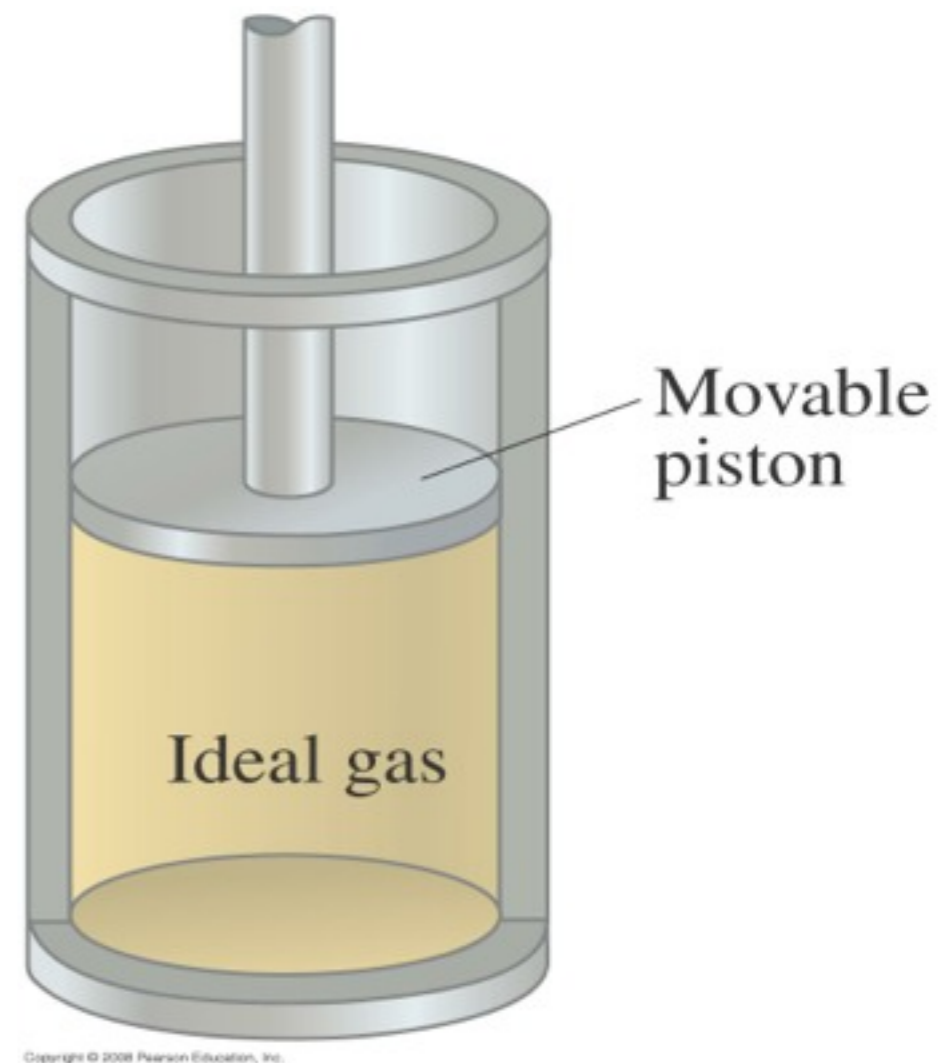
For a Carnot cycle $Q_H/Q_L = T_H/T_L$ so $Q_H/T_H - Q_L/T_L = 0$. Thus, if we approximate any reversible cycle (a) as an infinite sum of Carnot cycles as in (b), we see that the integral of dQ/T around a closed path is zero. This means that **entropy is a state variable** — like potential energy, the change in its value depends only on the initial and final states.



Analogy: Entropy and Volume

The fact that entropy S is a property that depends uniquely on the state of a system makes it useful. Like internal energy U , S is a property that is not obvious, but needs to be calculated from other properties of the system.

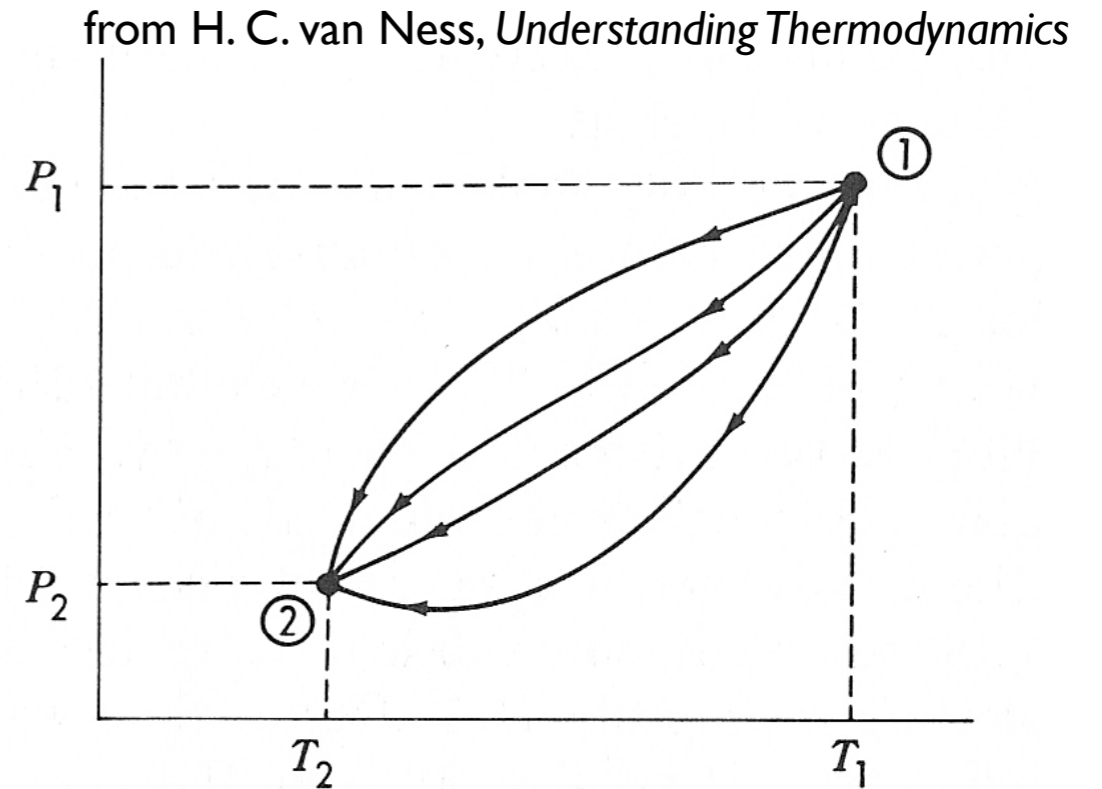
If volume V were such a non-obvious property, how could we discover it? Consider as the system an ideal gas in a cylinder confined by a piston. We would do reversible experiments and look for something that just depends on the change of state of the system.



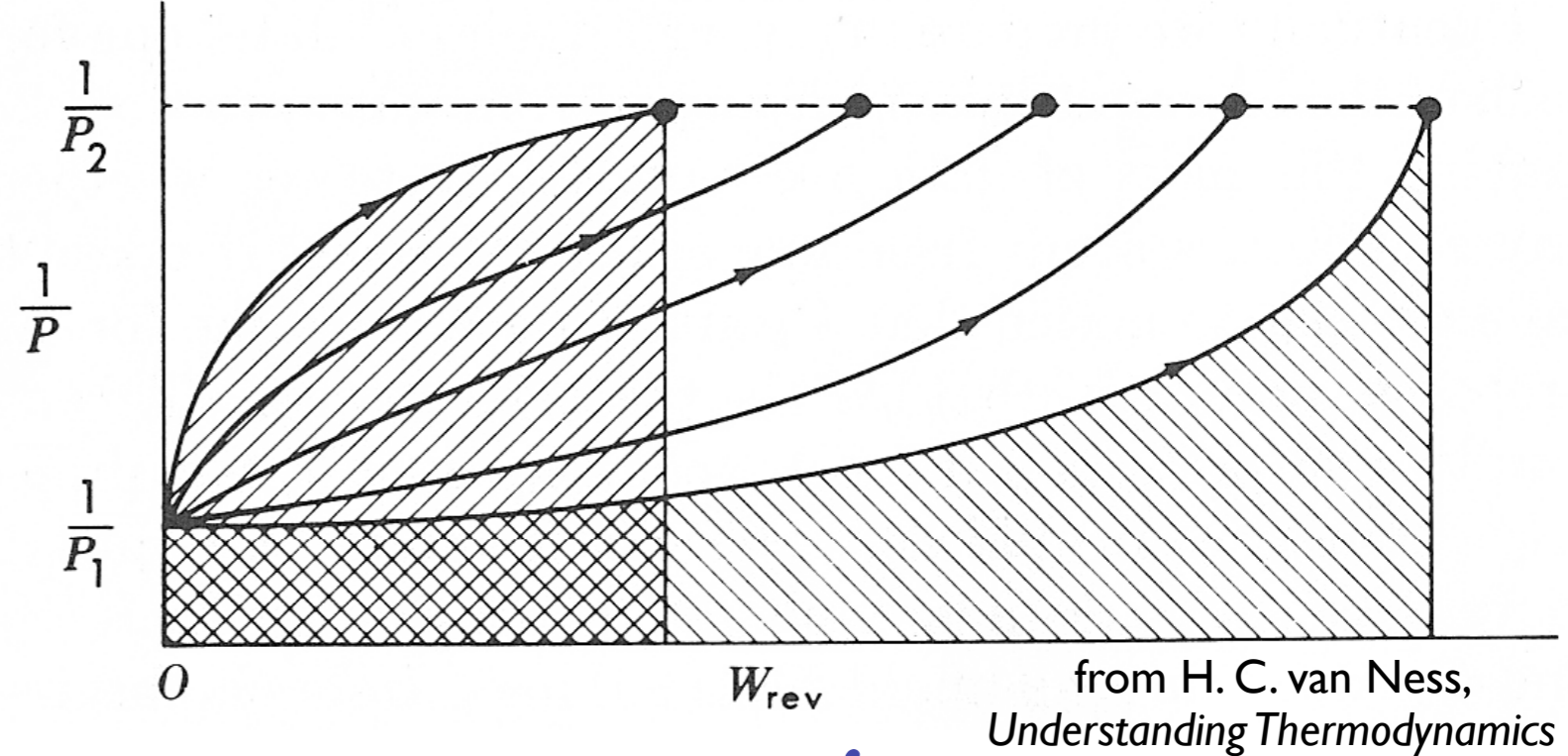
For example, we might take the system through many reversible paths from ① to ② in the P - T diagram at the right. We might notice that, although Q and W each have different values for each path.

$Q - W = \Delta U$ is always the same. Here U is the internal energy of the gas, and this equation is just energy conservation, i.e. the 1st Law of Thermodynamics.

Looking for more regularities, we might try plotting T vs. Q , P vs. Q , T vs. W , P vs. W , etc. Getting more desperate, we next try plotting reciprocals, for example $1/P$ vs. W . Plotting $1/P$ vs. W actually turns out to be really interesting, as the next slide shows.



Plotting $1/P$ vs. W for these reversible processes, we find out that the area under each curve is exactly the same!



The area under each curve is of course $\int (1/P) dW$, but since $dW = PdV$, the area under each curve is actually $\int (1/P) dW = \int (1/P) PdV = \int dV = \Delta V$. We have “discovered” a new state variable, the volume V .

Notice that the relation between P and W is similar to that between T and Q , so how we define the entropy $\int (1/T) dQ = \Delta S$ is analogous to $\int (1/P) dW = \Delta V$. In fact, we can rewrite the 1st Law

$$dU = dQ - dW = T dS - P dV.$$

Extensive vs. Intensive Variables

The volume, internal energy, and entropy have the property that if we double a system, each of them also doubles. Such a variable is called “extensive”. In contrast, if we double a system, the pressure and temperature are unchanged. Variables like these are called “intensive”. Thus writing the 1st Law as

$$dU = dQ - dW = T dS - P dV.$$

with each product on the rhs (intensive)x(extensive), is more symmetrical than, for example, writing it as

$$dU = dQ - dW = C_V dT - P dV.$$

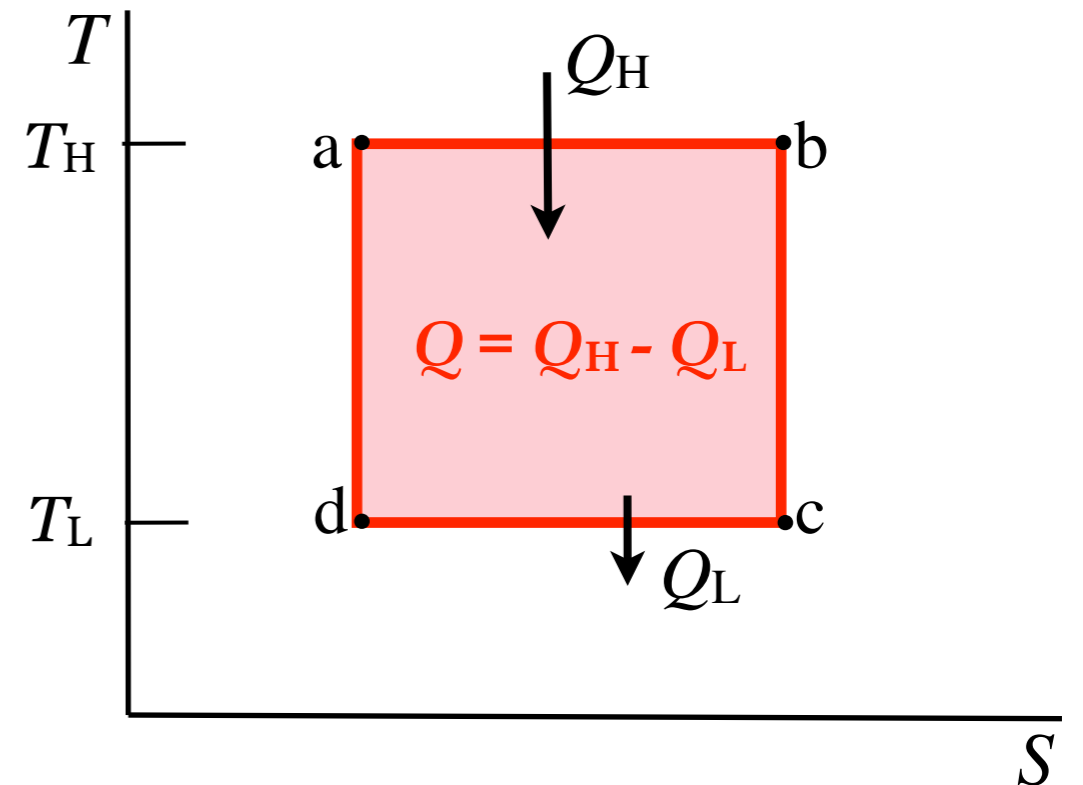
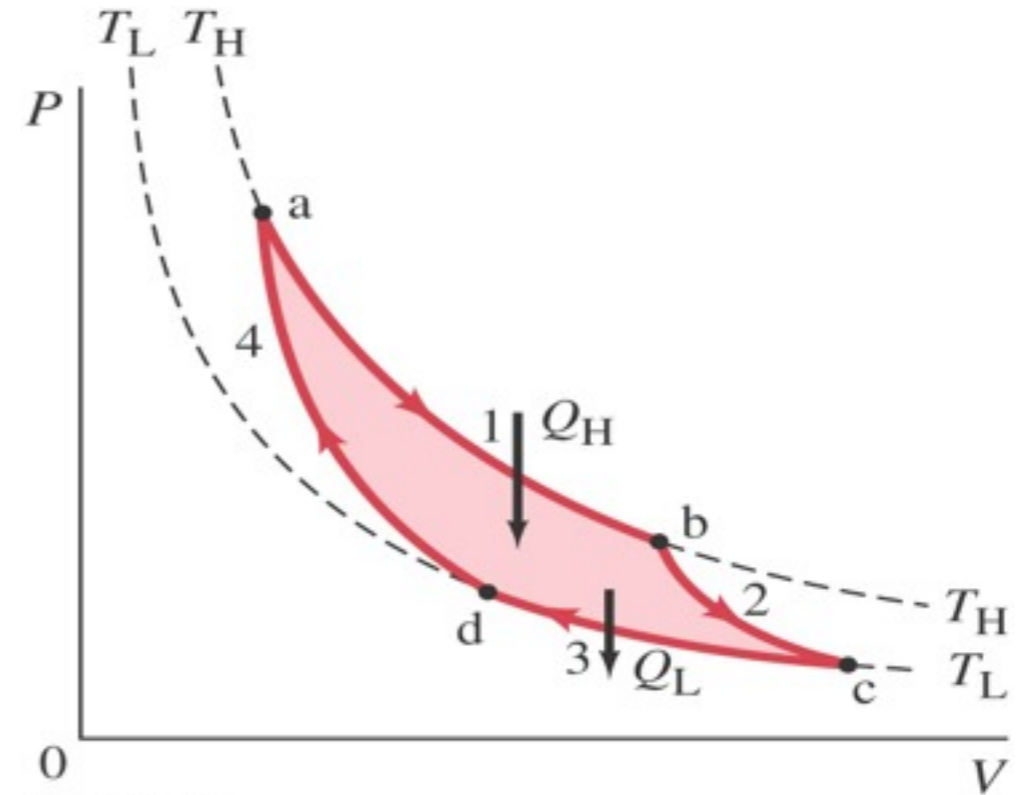
Perhaps one reason that entropy seems more abstract than energy is that there are many forms of energy (heat, chemical, electrical, etc.) but only “internal” entropy.

The Carnot cycle consists of:

- Isothermal expansion ab
- Adiabatic expansion bc
- Isothermal compression cd
- Adiabatic compression da

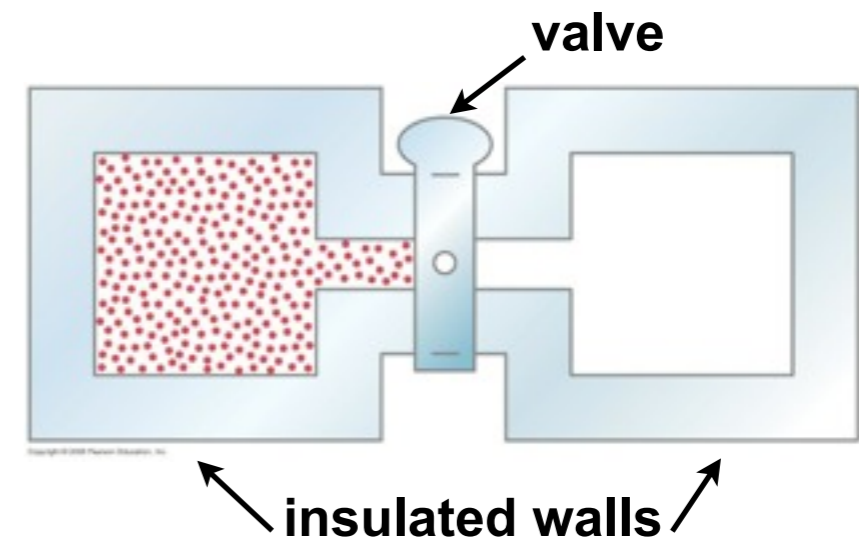
The area enclosed in the P - V diagram is the work W done in the cycle since $dW = P dV$.

We can alternatively draw the Carnot cycle in a T - S diagram. The area in the T - S diagram is the heat Q transferred since $dQ = T dS$. It is also the work done W , by energy conservation.



Example 20-7: Consider the adiabatic free expansion of 1.00 mole of an ideal gas from volume V_1 to volume $V_2 = 2.00 V_1$. Calculate the change in entropy ΔS .

Free expansion is an adiabatic process: when the valve is opened, the gas expands with no change in its internal energy: $W = 0$, $Q = 0$, so $\Delta E_{\text{int}} = 0 \Rightarrow$ for an ideal gas $\Delta T = 0$.



Solution: The process is irreversible, but we can calculate ΔS in a reversible isothermal expansion between the same two volumes, giving

$$\Delta S = \int dQ/T = \int_{V_1}^{V_2} PdV/T = R \int_{V_1}^{V_2} dV/V = R \ln(V_2/V_1) = R \ln 2 = 1.4 \text{ cal/K}$$

There is no heat flow to the environment, so the total entropy change is what we just calculated. Because the process is irreversible, $\Delta S > 0$.

20-6 Entropy and the Second Law of Thermodynamics

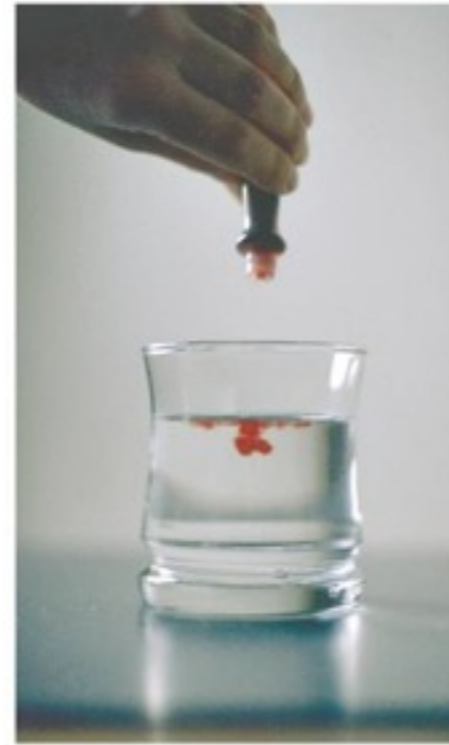
The fact that after every interaction the entropy of the system plus the environment increases is another way of putting the second law of thermodynamics:

The entropy of an isolated system never decreases. It either stays constant (reversible processes) or increases (irreversible processes).

20-7 Order to Disorder

Entropy is a measure of the **disorder** of a system. This gives us yet another statement of the second law: *Natural processes tend to move toward a state of greater disorder.* This gives an arrow of time.

Example: If you put a drop of dye in a beaker of water, it will spread out—but case (c) will never revert to case (a) spontaneously!



(a)



(b)



(c)

Thermal equilibrium is a similar process—the uniform final state has more disorder than the separate temperatures in the initial state.

Which has higher entropy – a mole of ideal gas at 20 °C occupying 10 liters or a mole of the same gas at 20 °C occupying 100 liters?

A. The gas in 10 liters

B. the gas in 100 liters

C. No difference

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C. No difference

How much higher entropy does a mole of ideal gas at 20 °C occupying 100 liters have compared to a mole of gas at 20 °C occupying 10 liters?

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To calculate this, consider a reversible isothermal expansion. Since the internal energy of an ideal gas depends only on T , it doesn't change in the expansion. Thus $dQ = dW = PdV$, and $P = nRT/V$, so

$$\Delta S = \int dQ/T = \int (nRT/V)dV/T = nR \ln(V_f/V_i)$$

Here $\Delta S = R \ln 10 = (2.0 \text{ cal/K})(2.3) = 4.6 \text{ cal/K}$.

20-8 Unavailability of Energy; Heat Death

Another consequence of the second law:

In any irreversible process, some energy becomes unavailable to do useful work.

If we look at the universe as a whole, it seems inevitable that, as more and more energy is converted to unavailable forms, the ability to do work anywhere will gradually vanish. This is called the “heat death of the universe”. We will come back to this in the last lecture, next week.

20-9 Statistical Interpretation of Entropy and the Second Law

Microstate: a particular configuration of atoms

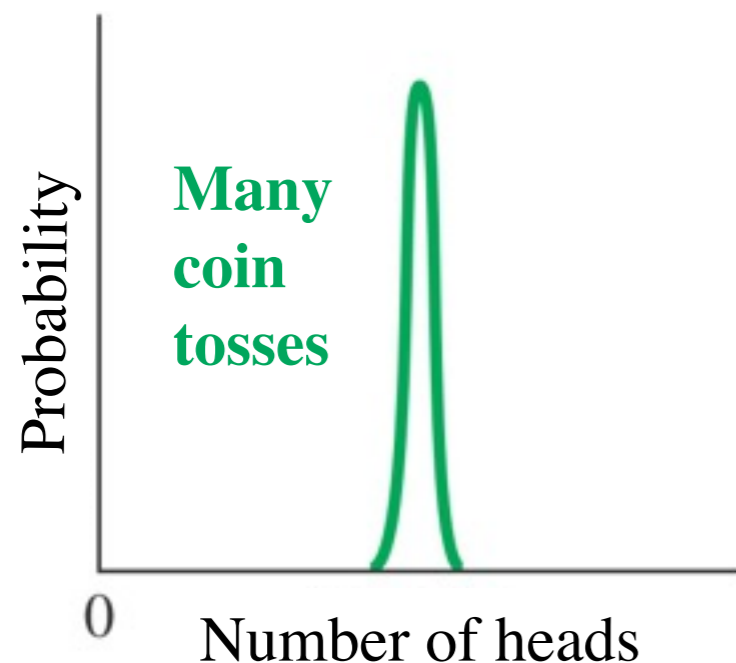
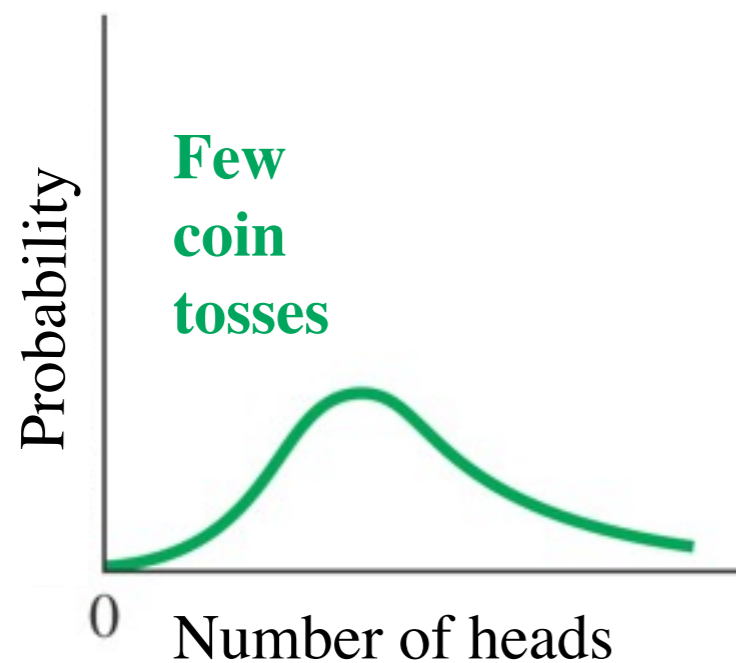
Macrostate: a particular set of macroscopic variables

This example uses coin tosses:

TABLE 20–1 Probabilities of Various Macrostates for 100 Coin Tosses

Macrostate		Number of Microstates	Probability
Heads	Tails		
100	0	1	7.9×10^{-31}
99	1	1.0×10^2	7.9×10^{-29}
90	10	1.7×10^{13}	1.4×10^{-17}
80	20	5.4×10^{20}	4.2×10^{-10}
60	40	1.4×10^{28}	0.01
55	45	6.1×10^{28}	0.05
50	50	1.0×10^{29}	0.08
45	55	6.1×10^{28}	0.05
40	60	1.4×10^{28}	0.01
20	80	5.4×10^{20}	4.2×10^{-10}
10	90	1.7×10^{13}	1.4×10^{-17}
1	99	1.0×10^2	7.9×10^{-29}
0	100	1	7.9×10^{-31}

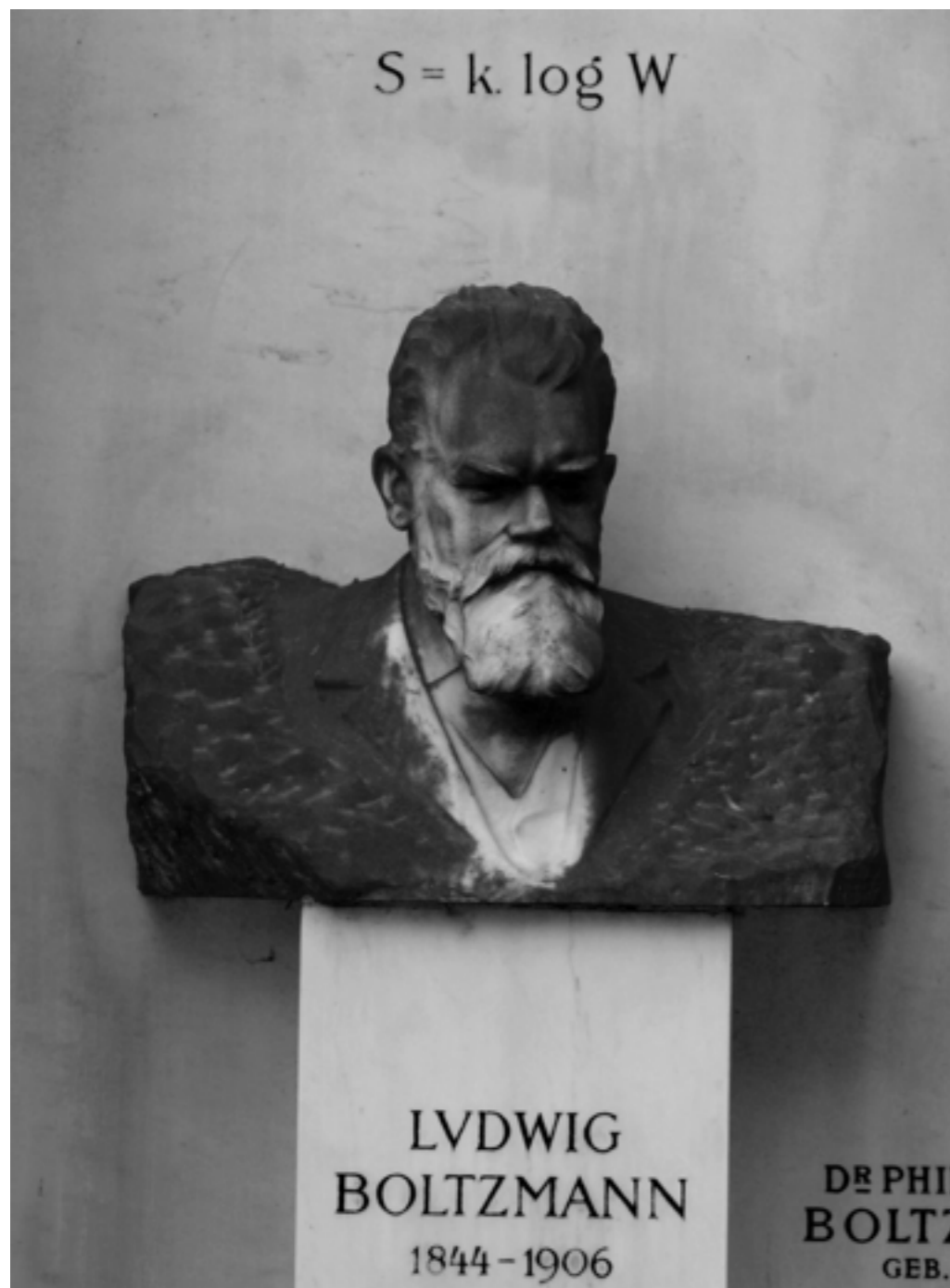
The more coin tosses, the more probable it is that the number of heads is about half. Similarly, for gas in a box, the most probable configuration is to have half the gas in each half of the box. Least probable: all in one half!



The most probable state is the one with the greatest disorder, or the greatest entropy. With k being Boltzmann's constant and \mathcal{W} the number of microstates, Boltzmann showed that the entropy is

$$S = k \ln \mathcal{W}.$$

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$$S = k \ln W.$$

← Boltzmann's tombstone, Vienna

Statistical determination of entropy: Determine the change in entropy for the adiabatic free expansion of one mole of an ideal gas as its volume increases by a factor of 10. Assume \mathcal{W} , the number of microstates for each macrostate, is the number of possible positions of the gas molecules.

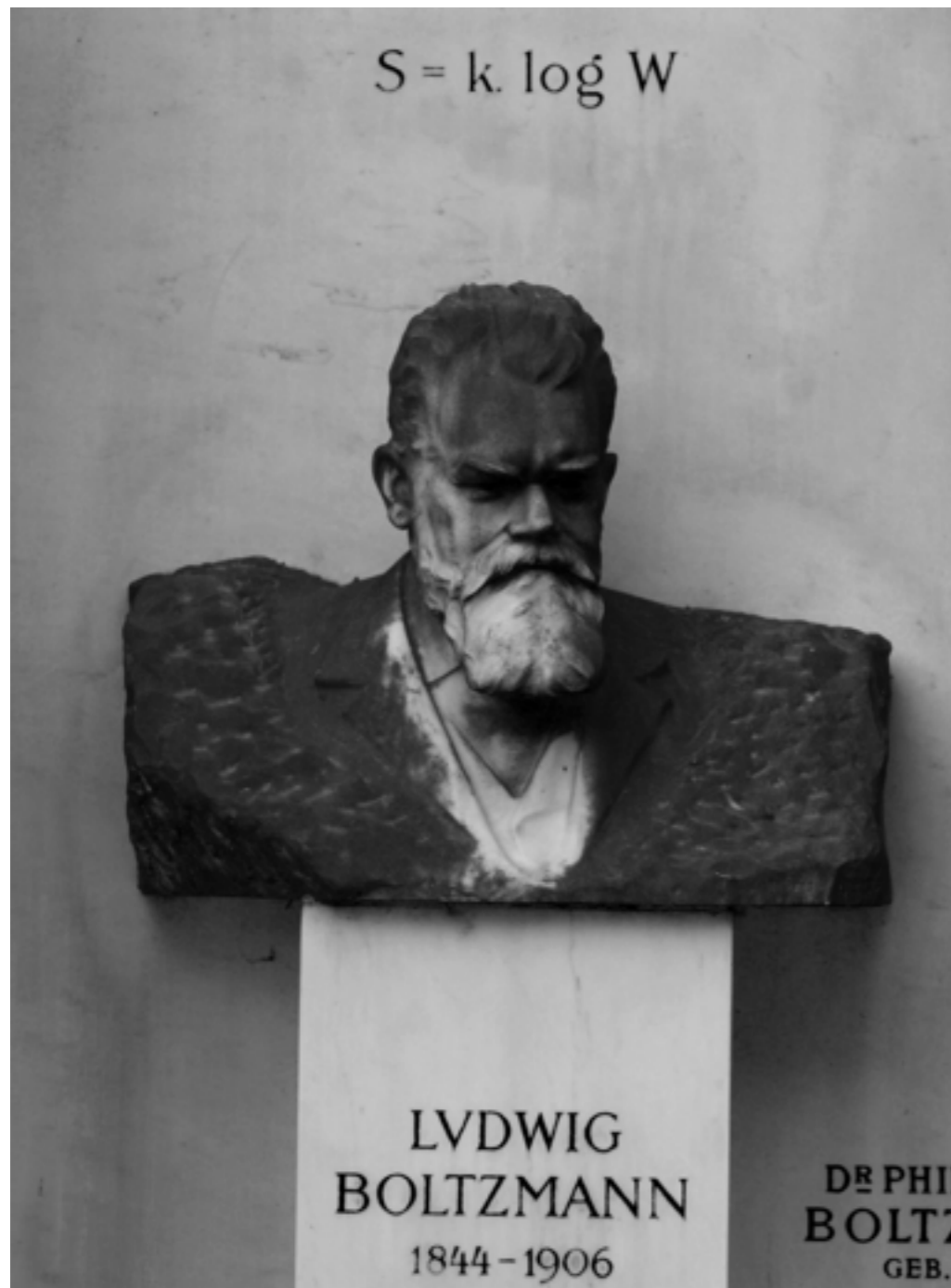
Statistical determination of entropy: Determine the change in entropy for the adiabatic free expansion of one mole of an ideal gas as its volume increases by a factor of 10. Assume \mathcal{W} , the number of microstates for each macrostate, is the number of possible positions of the gas molecules.

When the volume increases by a factor of 10, the number of positions of each molecule increases by the same factor. Thus the number of microstates increases by 10^{N_A} , where N_A = Avogadro's number. Then Boltzmann's formula for the entropy gives

$$\Delta S = k \ln 10^{N_A} = kN_A \ln 10 = R \ln 10$$

in agreement with our previous calculation!

The iconic form of the equation $S = k \log W$ on Boltzmann's tombstone is in fact due to Planck. As Planck wrote in his Nobel Prize lecture in 1920, “This constant is often referred to as Boltzmann's constant, although, to my knowledge, Boltzmann himself never introduced it.”



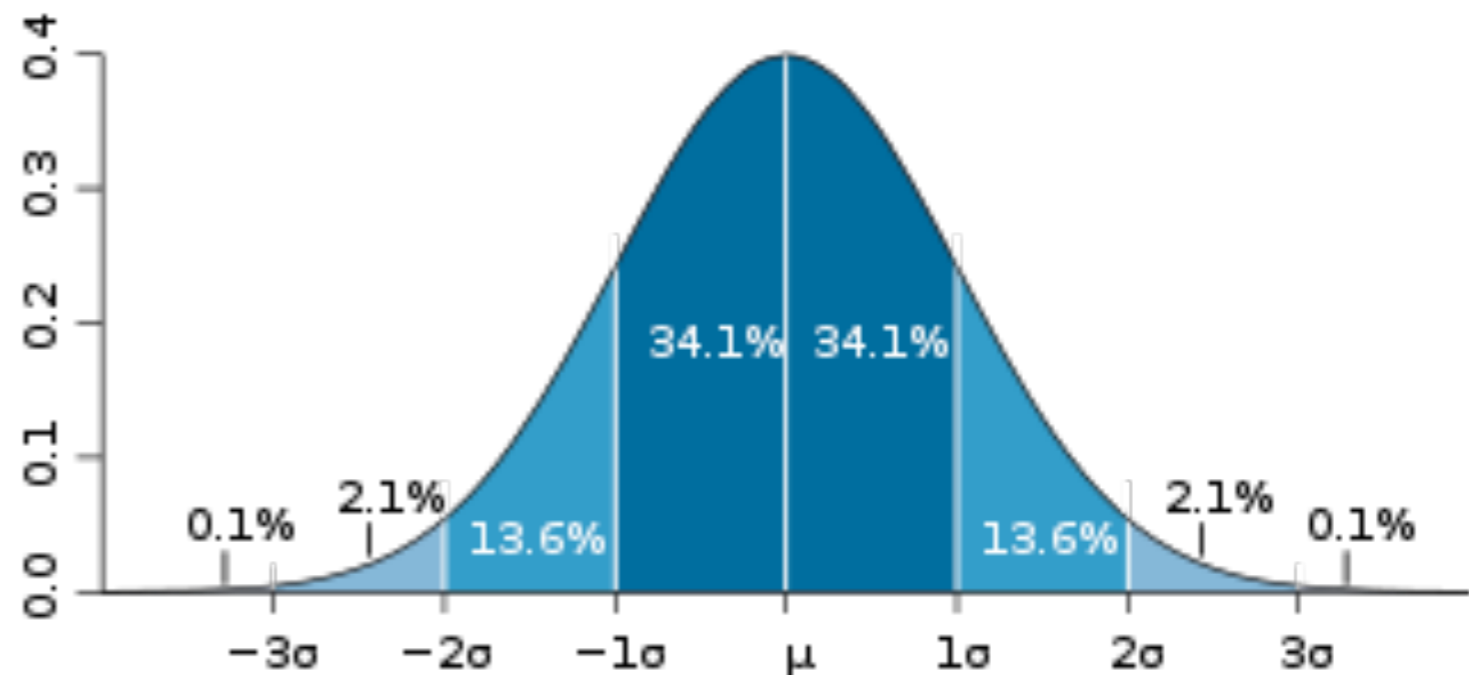
Boltzmann apparently never gave thought to the possibility of an exact measurement of k . Physicists disagreed in the second half of the nineteenth century as to whether atoms and molecules were real, as Boltzmann thought, or whether they were simply a useful tool for solving problems.

← Boltzmann's tombstone, Vienna

20-9 Statistical Interpretation of Entropy and the Second Law

In this form, the second law of thermodynamics does not forbid processes in which the total entropy decreases; it just makes them **extremely** unlikely.

The standard deviation from an equal distribution of gas molecules on either side of a box is $\Delta N = 1/(2\sqrt{N})$. For a mole of gas, this is $\sigma = \Delta N = 1/(2\sqrt{N_A}) = 6 \times 10^{-13}$. The probability of deviations from equal numbers is given by the bell-shaped curve. The probability of a 2σ (billionth) or greater deviation from equal numbers is only $\sim 2\%$.



20-10 Thermodynamic Temperature

Since the ratio of heats exchanged between the hot and cold reservoirs in a Carnot engine is equal to the ratio of temperatures $Q_H/Q_L = T_H/T_L$, Kelvin argued that we can define a thermodynamic temperature scale using the triple point of water:

$$T = (273.16\text{K})(Q/Q_{\text{tp}}).$$

Here, Q and Q_{tp} are the heats exchanged by a Carnot engine with reservoirs at temperatures T and T_{tp} .

Third Law of Thermodynamics

It is not possible to reach absolute zero in any finite number of processes.

Suppose that the temperature T of a substance can be reduced in an isentropic process by changing some parameter X from X_2 to X_1 . If there were an entropy difference at absolute zero, $T=0$ could be reached in a finite number of steps. However, at $T=0$ there is no entropy difference so an infinite number of steps would be needed, as shown in the Figure. The key idea of the 3rd Law is that entropy differences ΔS vanish at $T=0$. He^3/He^4 dilution refrigerators reach $T \sim 10^{-3}$ K and atomic cooling has now reached $T < 3 \times 10^{-12}$ K.

