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# Lecture 14. *Entropy*

- In this unit we will learn about
  - entropy!



entropy

<http://www.kierandkelly.com/what-is-complexity/history-of-entropy/>

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# Carnot Cycle

$$\oint \frac{dQ_{\text{rev}}}{T} = 0$$



$$\int_A^B \frac{dQ_{\text{rev}}}{T} \quad \text{Is path independent}$$

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# Adiabatic process



Entropy

- No change in entropy  $\rightarrow$  isentropic

# Irreversible changes

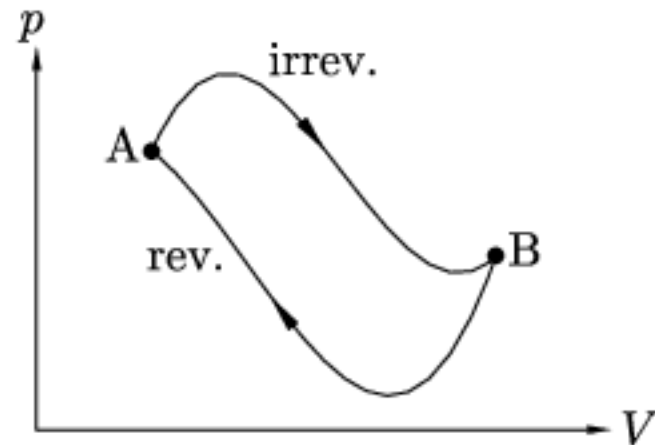
- State function, means integral over closed loop is zero

$$\oint \frac{dQ_{\text{rev}}}{T} = 0.$$

$$\oint \frac{dQ}{T} \leq 0 \quad \text{Clausius inequality}$$

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{\text{rev}}}{T} \leq 0.$$

$$\int_A^B \frac{dQ}{T} \leq \int_A^B \frac{dQ_{\text{rev}}}{T} \Rightarrow dS = \frac{dQ_{\text{rev}}}{T} \geq \frac{dQ}{T}$$



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# Thermally isolated system

$$dQ = 0$$

$$dS \geq 0$$

Any change for this thermally isolated system always results in the entropy:

- either staying the same (for a reversible change)
- or increasing (for an irreversible change).

This gives another statement of the second law, namely that: "**the entropy of an isolated system tends to a maximum.**"

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# Application to the universe

## Application to the Universe

Assuming that the Universe can be treated as an isolated system, the first two laws of thermodynamics become:

(1)  $U_{\text{Universe}} = \text{constant}$

(2)  $S_{\text{Universe}}$  can only increase



# Example

$$dS = \frac{dQ_{\text{rev}}}{T} \geq \frac{dQ}{T}$$

The heat transferred from the reservoir to the system is  $\Delta Q = C(T_R - T_S)$ , where  $C$  is the heat capacity of the system.



If  $T_R > T_S$ , heat is transferred from reservoir to system, the system warms and its **entropy increases**; the entropy of the reservoir decreases, because heat flows out of it.

If  $T_R < T_S$ , heat is transferred from system to reservoir, the system cools and its **entropy decreases**; the entropy of the reservoir increases, because heat flows into it.

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The entropy change in the reservoir, which has constant temperature  $T_R$ , is

$$\Delta S_{\text{reservoir}} = \int \frac{dQ}{T_R} = \frac{1}{T_R} \int dQ = \frac{\Delta Q}{T_R} = \frac{C(T_S - T_R)}{T_R}$$

while the entropy change in the system is

Hence, the total entropy change in the Universe is

We see that always have that



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# Back to first law

$$dU = \bar{d}Q + \bar{d}W.$$

Reversible changes:  $\bar{d}Q = TdS$   
 $\bar{d}W = -pdV.$   $\Rightarrow dU = TdS - pdV.$

**This equation is ok for irreversible changes as well!**

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This equation implies that the internal energy  $U$  changes when either  $S$  or  $V$  changes. Thus, the function  $U$  can be written in terms of the variables  $S$  and  $V$  which are its **natural variables**. These variables are both extensive (i.e., they scale with the size of the system).

The variables  $p$  and  $T$  are both intensive (i.e., they do not scale with the size of the system). In fact, since mathematically we can write  $dU$  as

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad \Rightarrow \quad \begin{aligned} T &= \left(\frac{\partial U}{\partial S}\right)_V \text{ and} \\ p &= -\left(\frac{\partial U}{\partial V}\right)_S. \end{aligned}$$

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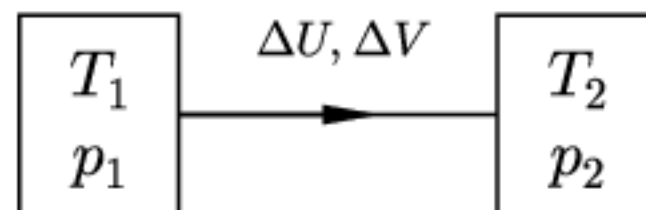
The ratio of  $p$  and  $T$  can also be written in terms of the variables  $U, S$  and  $V$ , as follows:

$$\frac{p}{T} = - \left( \frac{\partial U}{\partial V} \right)_S \left( \frac{\partial S}{\partial U} \right)_V$$

using the reciprocal theorem and

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Two systems, with pressures  $p_1$  and  $p_2$  and temperatures  $T_1$  and  $T_2$ . If internal energy  $\Delta U$  is transferred from system 1 to system 2 and volume  $\Delta V$  is transferred from system 1 to system 2, what is the change of entropy?



$$dS = \frac{1}{T}dU + \frac{p}{T}dV$$

The change in entropy is then straightforwardly

Entropy always increases in any physical process. Thus, when equilibrium is achieved, the entropy will have achieved a maximum, so that

This means that the joint system cannot increase its entropy by further exchanging volume or internal energy between system 1 and system 2 . can only be achieved when and

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# Summary

$dU = \delta Q + \delta W$  always true

only true for reversible changes

only true for reversible changes

always true

For irreversible changes:

# Joule Expansion of ideal gas

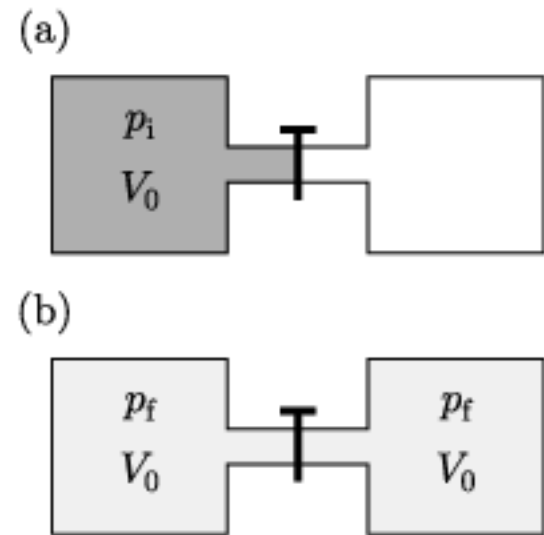
$$p_i V_0 = RT_i \quad \text{Initially}$$

$$p_f (2V_0) = RT_f \quad \text{Finally}$$

$$\Delta U = 0. \quad \text{System is isolated}$$

$$\Delta T = 0 \quad \text{Since } U \text{ only depends on } T \text{ for an ideal gas}$$

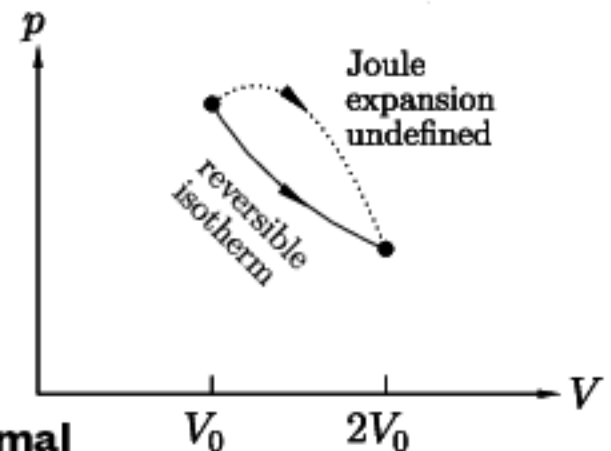
$$p_i V_0 = p_f (2V_0) \implies p_f = \frac{p_i}{2}$$



# Joule Expansion: entropy change

The pressure and volume of the system are undefined during the process immediately after the partition is removed since the gas is in a **non-equilibrium** state.

However, entropy is a function of state and we can take another route from the initial state to the final state since changes of functions of state are independent of the route taken.



**We can calculate the change in entropy for a reversible isothermal expansion of the gas from volume  $V_0$  to volume  $2V_0$ .**

Since the internal energy is constant in the isothermal expansion of an ideal gas,  $dU = 0$ , and hence the first law gives us  $TdS = pdV$ , so that

$$\Delta S = \int_i^f dS = \int_{V_0}^{2V_0} \frac{pdV}{T} = \int_{V_0}^{2V_0} \frac{RdV}{V} = R \ln 2$$

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## Change of entropy in the gas, surroundings, and Universe during a Joule expansion?

For the **reversible isothermal** expansion of the gas, we deduce the change of entropy in the surroundings so that the entropy in the Universe does not increase (because we are dealing with a reversible situation).

$$\begin{aligned}\Delta S_{\text{gas}} &= R \ln 2 \\ \Delta S_{\text{surroundings}} &= -R \ln 2 \\ \Delta S_{\text{Universe}} &= \Delta S_{\text{gas}} + \Delta S_{\text{surroundings}} = 0\end{aligned}$$



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Once the Joule expansion has occurred, you can only put the gas back in the left-hand side by compressing it. The best (less work) you can do is to do this reversibly, by a reversible isothermal compression, which takes work  $\Delta W$  given (for 1 mole of gas) by

$$\Delta W = - \int_{2V_0}^{V_0} p dV = - \int_{2V_0}^{V_0} \frac{RT}{V} dV = RT \ln 2 = T \Delta S_{\text{gas}}$$

The increase of entropy in a Joule expansion is thus

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In the Joule expansion, the system is thermally isolated so no heat can be exchanged:  $\Delta Q = 0$ .

No work is done:  $\Delta W = 0$

- Hence  $\Delta U = 0$  (so for an ideal gas,  $\Delta T = 0$ ).

But if  $\Delta Q = 0$ , doesn't that imply that  $\Delta S = \Delta Q/T = 0$ ?

The above reasoning is correct, until the very end: the answer to the question in the last point is NO! The equation  $dQ = TdS$  is only true for reversible changes. In general  $dQ = TdS + PdV$  and here we have  $dV \neq 0$  and  $dQ = 0$ .

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# Statistical origin for entropy

- We have a definition of entropy in terms of thermodynamics. Can we get an understanding using statistics?

$$T = \left( \frac{\partial U}{\partial S} \right)_V$$

- That is:  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V \implies S = k_B \ln \Omega$   
 $\frac{1}{k_B T} = \frac{d \ln \Omega}{dE}$

This is the expression for the entropy of a system that is in a particular macrostate in terms of  $\Omega$ , the number of microstates associated with that macrostate.

*We are assuming that the system is in a particular macrostate with fixed energy, and this situation is known as the microcanonical ensemble.*

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# Joule expansion revisited

Following a Joule expansion, each molecule can be either on the left-hand side or the right-hand side of the container. For each molecule there are therefore two ways of placing it. For one mole ( $N_A$  molecules) there are  $2^{N_A}$  ways of placing them.

The number of microstates associated with the gas being in a container twice as big as the initial volume is larger by a multiplicative factor

$$2^{N_A}$$

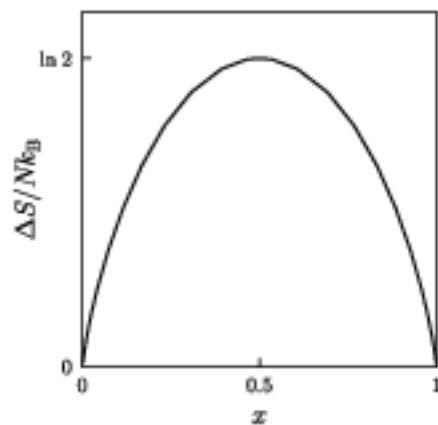
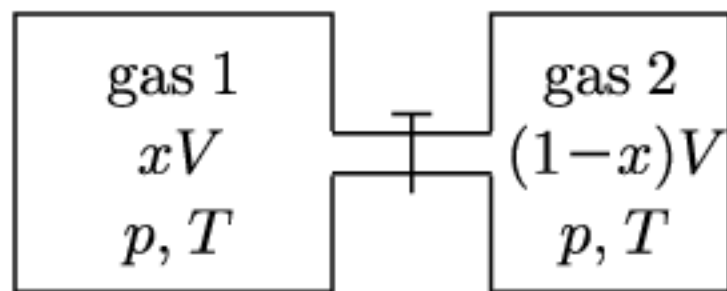
so that the additional entropy is

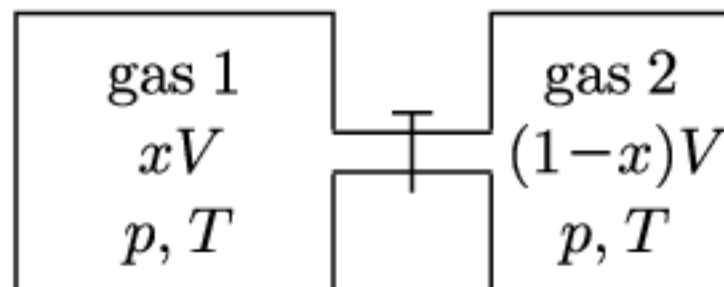
# Entropy of mixing

- If  $N$  is the total number of molecules, there are  $xN$  molecules of type 1 and  $(1-x)N$  molecules of type 2.
- Entropy of mixing comes from the mixture of the two gases.
- We can see this as 2 Joule mixing processes
- For isothermal process, the internal energy does not change and  $TdS = pdV$  and  $dS = Nk_B dV/V$
- The entropy of mixing is thus

$$\Delta S = xNk_B \int_{xV}^V \frac{dV_1}{V_1} + (1-x)Nk_B \int_{(1-x)V}^V \frac{dV_2}{V_2}$$

That is: 
$$\Delta S = -Nk_B(x \ln x + (1-x) \ln(1-x))$$

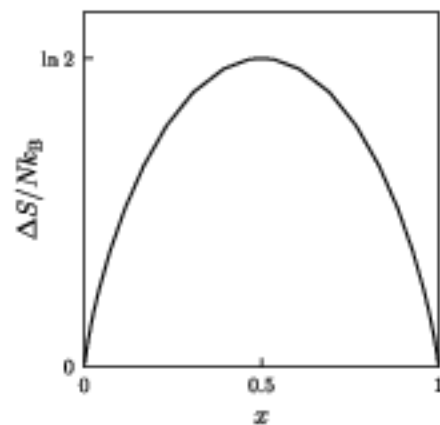




No entropy increase when  $x = 0$  or  $x = 1$ .

The maximum entropy change occurs when  $x = \frac{1}{2}$ , in which case  $\Delta S = Nk_B \ln 2$ . (corresponds to the equilibrium state in which no further increase of entropy is possible)

This expression for  $x = \frac{1}{2}$  also admits to a very simple statistical interpretation. Before the mixing of the gases takes place, we know that gas 1 is only in the first vessel and gas 2 is only in the second vessel. After mixing, each molecule can exist in additional "microstates"; for every microstate with a molecule of gas 1 on the left there is now an additional one with a molecule of gas 1 now on the right. Therefore  $\Omega$  must be multiplied by  $2^N$  and hence  $S$  must increase by  $k_B \ln 2^N$ , which is  $Nk_B \ln 2$



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# Paradox?

This treatment has a profound consequence: **distinguishability** is an important concept!

We have assumed that there is some tangible difference between gas 1 and gas 2, so that there is some way to label whether a particular molecule is gas 1 or gas 2.

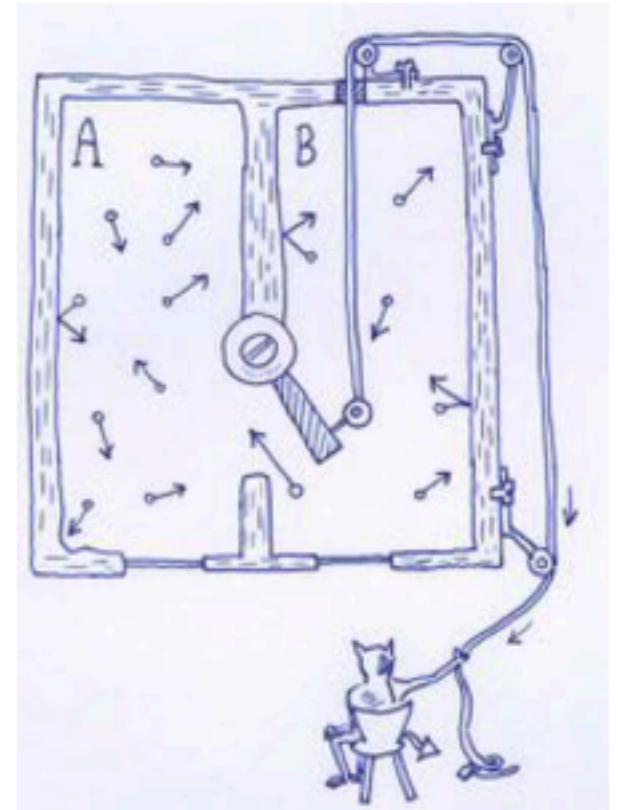
But what if the two gases were actually the same? Physically, we would expect that mixing them would have no observable consequences, so there should be no increase in entropy. **Thus mixing should only increase entropy if the gases really are distinguishable.**

# Maxwell's demon

In 1867, James Clerk Maxwell came up with an intriguing puzzle via a thought experiment.

We start with a Joule expansion on a gas.

- A gas is initially in one chamber, which is connected via a closed tap to a second chamber containing only a vacuum; The tap is opened and the gas in the first chamber expands to fill both chambers.
- **Equilibrium** is established and the pressure in each chamber is now half of what it was in the first chamber at the start. (this is an irreversible process)



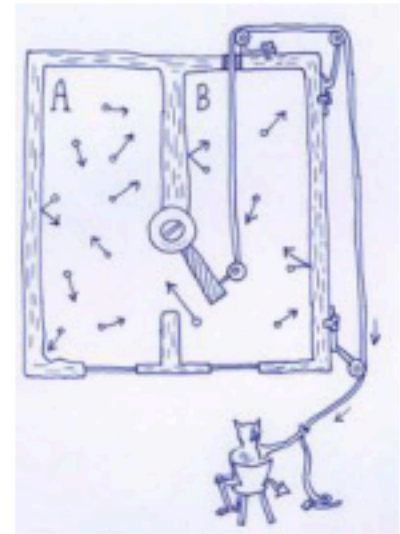


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# Maxwell's demon

Maxwell imagined that the tap was operated by a microscopic intelligent creature, now called **Maxwell's demon**, who was able to watch the individual molecules bouncing around close to the tap.

- If the demon sees a gas molecule heading from the second chamber back into the first, it quickly opens the tap and then shuts it straight away, just letting the molecule through.
- If it spots a gas molecule heading from the first chamber back into the second chamber, it keeps the tap closed.
- The demon does no work and yet it can make sure that the gas molecules in the second chamber all go back into the first chamber.
- Thus it creates a pressure difference between the two chambers where none existed before the demon started its mischief.



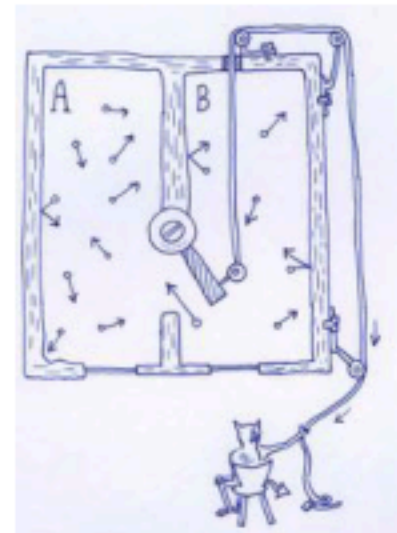
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# Maxwell's demon

It looks as if the demon could therefore cause entropy to decrease in a system with no consequent increase in entropy anywhere else. In short, Maxwell's demon appears to make a mockery out of the second law of thermodynamics. How on earth does it get away with it?

One early idea was that the demon needs to make measurements of where all the gas molecules are, and to do this would need to shine light on the molecules. thus the process of observation of the molecules might be thought to rescue us from Maxwell's demon. However, this idea turned out not to be correct as it was found to be possible, even in principle, to detect a molecule with arbitrarily little work and dissipation.

Remarkably, it turns out that because a demon needs to have a memory to operate (so that it can remember where it has observed a molecule and any other results of its measurement process), this act of storing information is associated with an increase of entropy, and this increase cancels out any decrease in entropy that the demon might be able to effect in the system.



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# Entropy of information

The demon is in fact a type of computational device that processes and stores information about the world. It is possible to design a computational process that proceeds entirely reversibly, and therefore has no increase in entropy associated with it. However, the act of erasing information is irreversible. Erasing information always has an associated increase in entropy (of  $k_B \ln 2$  per bit); Maxwell's demon can operate reversibly therefore, but only if it has a large enough hard disc that it doesn't ever need to clear space to continue operating. The Maxwell demon therefore beautifully illustrates the connection between entropy and information.

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# Entropy and probability

The entropy that you measure is due to the number of different states in which the system can exist, according to  $S = k_B \ln \Omega$ .

However, each state may consist of a large number of microstates that we can't directly measure.

Since the system could exist in any one of those microstates, there is extra entropy associated with them.

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# Example

A system has five possible equally likely states in which it can exist, and which of those states it occupies can be distinguished by some easy physical measurement. The entropy is therefore, using

$$S = k_B \ln 5$$

However, each of those five states is made up of three equally likely microstates and it is not possible to measure easily which of those microstates it is in. The extra entropy associated with these microstates is  $k_B \ln 3$ . The system therefore really has  $15$  states and the total entropy is therefore  $k_B \ln 15$ . This can be decomposed into

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Now let us suppose that a system can have  $N$  different, equally likely microstates.

These microstates are divided into various groups (we will call these groups macrostates with  $n_i$  microstates contained in the  $i$  th macrostate).

We must have that the sum of all the microstates in each macrostate is equal to the total number of microstates, so that

$$\sum_i n_i = N$$

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$S_{\text{tot}}$  is equal to the sum of the entropy associated with being able to be in different macrostates, which is our measured entropy  $S$ , and the entropy  $S_{\text{micro}}$  associated with it being able to be in different microstates within a macrostate:

$$S_{\text{tot}} = S + S_{\text{micro}}$$

The entropy associated with being able to be in different microstates (the aspect we can't measure) is given by

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**Entropy for a system with  $\Omega$  macrostates,  
each with probability  $P_i = 1/\Omega$**

$$= -k_B \ln \frac{1}{\Omega}$$

\*We assume the microcanonical ensemble



# Summary

- **Entropy**

- Entropy is defined by  $dS = dQ_{\text{rev}}/T$
- The statistical definition of entropy is
- The general definition of entropy, due to **Gibbs**, is
- The entropy of an isolated system tends to a maximum (attained at equilibrium).

- The **laws of thermodynamics** can be stated as follows:

- (1)  $\Delta S_{\text{univ}} \geq 0$  constant.
- (2)  $\Delta S_{\text{univ}} > 0$  can only increase.

- These can be combined to give  $\Delta S_{\text{univ}} \geq 0$  which **always holds**.