LIVE INTERACTIVE LEARNING @ YOUR DESKTOP

ENTROPY, ENERGY, and TEMPERATURE

Presented by: Jerry Bell, Pat Deibert and Bonnie Bloom

December 15, 2010
6:30 p.m. - 8:00 p.m. Eastern time
ENTROPY, ENERGY, and TEMPERATURE

Energy Exchange

Jerry Bell, ACS (retired)
Bonnie Bloom, Hilliard Davidson HS, OH
Pat Deibert, Sheboygan Falls HS, WI
Entropy, Energy, and Temperature

Quiz: What is likely to be the result, if two identical blocks of copper metal, one hot and the other cold, are brought together and allowed to exchange energy before separating again.

A

Colder

Hotter

B

Warm

Warm

C

Hot

Cold
Entropy, Energy, and Temperature

Quiz: What is likely to be the result, if two identical blocks of copper metal, one hot and the other cold, are brought together and allowed to exchange energy before separating again.

How general is this result?

→ B
Activity: Gather your cup of warm water and second cup of an equal volume of cool water. Take and record the temperature of the warm water and then of the cool water. While the thermometer is still in the cool water, pour in all the warm water and stir until the temperature is constant. Pat does a similar experiment in this video.
Activity: Gather your cup of warm water and second cup of an equal volume of cool water. Take and record the temperature of the warm water and then of the cool water. While the thermometer is still in the cool water, pour in all the warm water and stir until the temperature is constant.

Result: The final temperature is

A. lower than that of the cool water.
B. higher than that of the warm water.
C. intermediate between the warm and cool water temperatures.
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B. higher than that of the warm water.
C. intermediate between the warm and cool water temperatures.

Our experience is that the spontaneous direction of energy exchange is from the warmer to the cooler body. Whatever model we propose to explain energy exchange must be consistent with this experience.
Entropy, Energy, and Temperature

The Direction of Change
Entropy, Energy, and Temperature

Model for change from previous Web Seminar--Entropy: Mixing and Oil Spills--restated in terms of energy:
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Entropy, Energy, and Temperature

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If a system can exist in more than one observable state (hot-cold or warm-warm, for example), spontaneous changes will be in the direction toward the state that is most probable.

The number of distinguishable arrangements, $W$, of the energy that give a particular state of a system is a measure of the probability that this state will be observed.
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The number of distinguishable arrangements, $W$, of the energy that give a particular state of a system is a measure of the probability that this state will be observed.

**Fundamental assumption**: Each distinguishably different energy arrangement of a system is equally probable.

Two arrangements are distinguishable if you can tell them apart. Exchanging identical objects does not produce a new arrangement.
Questions?
Entropy, Energy, and Temperature

Energy at the Molecular Scale
Entropy, Energy, and Temperature

Thermal energy in a solid sample:

The atomic cores in a piece of copper metal are fixed in space in a sea of delocalized electrons, but vibrate according to how much thermal energy there is in the system, as in this animation.
Entropy, Energy, and Temperature

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All energy is quantized, that is, comes only in discrete packets.
Entropy, Energy, and Temperature

Thermal energy in a solid sample:

The atomic cores in a piece of copper metal are fixed in space in a sea of delocalized electrons, but vibrate according to how much thermal energy there is in the system, as in this animation.

All energy is quantized, that is, comes only in discrete packets.

Thermal energy can be transferred to and from a sample of metal like this in quantized amounts that are characteristic of the particular metal and atomic structure.
Entropy, Energy, and Temperature

Focus on the possible arrangements of energy in a tiny sample, four atoms, of copper metal.
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Each atom can vibrate in place and its vibrational energy is quantized. It can have any number of quanta of energy (shown like this to represent vibrational energy).
Entropy, Energy, and Temperature

Focus on the possible arrangements of energy in a tiny sample, four atoms, of copper metal.

Each atom can vibrate in place and its vibrational energy is quantized. It can have any number of quanta of energy (shown like this to represent vibrational energy).

For example, the third atom could be vibrating with one quantum of energy, while the others have none.
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Each atom can vibrate in place and its vibrational energy is quantized. It can have any number of quanta of energy (shown like this to represent vibrational energy).

For example, the third atom could be vibrating with one quantum of energy, while the others have none.

Quiz: How many distinguishable arrangements, $W_{1,4}$, are there for one quantum among the four atoms?  
A = 1  B = 2  C = 3  D = 4
Entropy, Energy, and Temperature

The four distinguishable arrangements, $W_{1,4}$, for one quantum among the four atoms are:

- $(1,0,0,0)$
- $(0,1,0,0)$
- $(0,0,1,0)$
- $(0,0,0,1)$
Entropy, Energy, and Temperature

Questions?
Adding More Energy
Entropy, Energy, and Temperature

How many distinguishable arrangements, $W_{2,4}$, are there for two quanta among the four atoms? Two arrangements are:

(0,2,0,0)

(0,1,0,1)

Quiz: What is another distinguishable arrangement of two quanta among four atoms, where each atom can have any number of quanta? Place a stamp twice on one atom or once each on two atoms where you want to place quanta.
Entropy, Energy, and Temperature

Number of distinguishable arrangements for two quanta among the four atoms: $W_{2,4} = 10$

- (2,0,0,0)
- (0,2,0,0)
- (0,0,2,0)
- (0,0,0,2)
- (1,1,0,0)
- (1,0,1,0)
- (1,0,0,1)
- (0,1,1,0)
- (0,1,0,1)
- (0,0,1,1)
Entropy, Energy, and Temperature

For a system of $n$ identical objects (quanta) allowed to occupy any of $N$ boxes (atoms), any number of objects per box, the number of distinguishable arrangements, $W_{n,N}$ is given by

$$W_{n,N} = \frac{(N+n-1)!}{(N-1)!n!}$$
Entropy, Energy, and Temperature

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\[
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\]

\[
W_{2,4} = \frac{5!}{(3!)2!} = \frac{5 \cdot 4 \cdot (3!)}{2 \cdot 1 \cdot (3!)} = \frac{5 \cdot 4}{2 \cdot 1} = \frac{5 \cdot 2}{1} = 5 \cdot 2 = 10
\]
Entropy, Energy, and Temperature

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Quiz: What is the number of distinguishable arrangements, $W_{6,4}$, for 6 quanta distributed among the 4 atoms in the solid?

$$W_{6,4} =$$
Entropy, Energy, and Temperature

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\]

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W_{2,4} = \frac{5!}{(3!)^2} = \frac{5 \cdot 4 \cdot (3!)}{2 \cdot 1 \cdot (3!)} = \frac{5 \cdot 4}{2 \cdot 1} = \frac{5 \cdot 2}{1} = 5 \cdot 2 = 10
\]

Quiz: What is the number of distinguishable arrangements, \( W_{6,4} \), for 6 quanta distributed among the 4 atoms in the solid?

\[
W_{6,4} = \frac{9!}{(3!)^6} = \frac{9 \cdot 8 \cdot 7 \cdot (6!)}{3 \cdot 2 \cdot 1 \cdot (6!)} = \frac{3 \cdot 4 \cdot 7}{1} = 84
\]

Take a moment to copy this table for later use in the seminar.

<table>
<thead>
<tr>
<th>( n )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W_{n,4} )</td>
<td>1</td>
<td>4</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>56</td>
<td>84</td>
</tr>
</tbody>
</table>
Quiz: Consider these two identical pieces of copper, one with 2 quanta of energy and the other with 6. What *observable* property is different for the two pieces?

A. Energy  
B. Entropy  
C. Temperature  
D. Atomic motion
Entropy, Energy, and Temperature

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If one object has more energy than another identical object, the one with more energy will have a higher *temperature*. Also, the atoms or molecules will be moving with higher average speed and the entropy will be higher, but these are not *observable* properties.
Quiz: Consider these two identical pieces of copper, one with 2 quanta of energy and the other with 6. What observable property is different for the two pieces?

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If one object has more energy than an another identical object, the one with more energy will have a higher temperature. Also, the atoms or molecules will be moving with higher average speed and the entropy will be higher, but these are not observable properties.

The total number, $W_{\text{total}}$, of distinguishable arrangements for this system is

$$W_{\text{total}} = W_{2,4} \cdot W_{6,4} = 10 \cdot 84 = 840$$
Entropy, Energy, and Temperature

Questions?
Entropy, Energy, and Temperature

Energy Exchange
Entropy, Energy, and Temperature

Quiz:

What would happen if the metals collided, two quanta were exchanged, and the metals separated?

A. Four quanta would be distributed over each group of four atoms in such a way that the total number of arrangements would be <840.

B. Four quanta would be distributed over each group of four atoms in such a way that the total number of arrangements would be =840.

C. Four quanta would be distributed over each group of four atoms in such a way that the total number of arrangements would be >840.
This is one of the 1225 distinguishable arrangements of quanta in the system after two quanta have been transferred from the hotter to the colder piece of copper.

\[ W_{\text{total}} = W_{4,4} \cdot W_{4,4} = 35 \cdot 35 = 1225 \]
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\[ W_{\text{total}} = W_{4,4} \cdot W_{4,4} = 35 \cdot 35 = 1225 \]

Although the number of distinguishable arrangements for the hotter piece decreased in the energy transfer, this was more than offset by the increase for the colder piece, so \( W_{\text{total}} \) after the transfer (1225) is larger than before the transfer (840). The transfer of energy from the hotter to colder body is favored and is observed for actual processes in the macroscopic world.
Entropy, Energy, and Temperature

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Both pieces of copper now have the same energy (same number of energy quanta), so their temperatures are the same and intermediate between the original temperatures as is also observed macroscopically.
Entropy, Energy, and Temperature

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\[ W_{\text{total}} = W_{4,4} \cdot W_{4,4} = 35 \cdot 35 = 1225 \]

Quiz: What would \( W_{\text{total}} \) be if only one quantum had been transferred? Does this make sense?
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Quiz: What would \( W_{\text{total}} \) be if only one quantum had been transferred? Does this make sense?.

\[ W_{\text{total}} = W_{3,4} \cdot W_{5,4} = 20 \cdot 56 = 1120 \]

\[ W_{2,4} \cdot W_{6,4} [840] < W_{3,4} \cdot W_{5,4} [1120] < W_{4,4} \cdot W_{4,4} [1225] \]

As energy is transferred from the hotter to the colder body, the number of arrangements (probability) increases until the temperatures are the same. Reaching a common temperature is observed experimentally for such a system. The model makes sense.
Entropy, Energy, and Temperature

Questions?
Entropy, Energy, and Temperature

Entropy Change in Energy Exchange
Entropy, Energy, and Temperature

Consider the entropy change, $\Delta S$, in a process, where $S \equiv k \cdot \ln W$

$$\Delta S \equiv S_{\text{final}} - S_{\text{initial}}$$
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$$\Delta S \equiv S_{\text{final}} - S_{\text{initial}} = k \cdot \ln W_{\text{final}} - k \cdot \ln W_{\text{initial}} = k \cdot \ln \left( \frac{W_{\text{final}}}{W_{\text{initial}}} \right)$$
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If $W_{\text{final}} > W_{\text{initial}}$, then $k \cdot \ln \left( \frac{W_{\text{final}}}{W_{\text{initial}}} \right) > 0$ and $\Delta S > 0$

That is, $\Delta S > 0$ for changes that are favored to occur.
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That is, $\Delta S > 0$ for changes that are favored to occur.

Apply these ideas to the energy transfer process just analyzed.

$$\Delta S_{(\text{cold} \rightarrow \text{warm})} = k \cdot \ln \left( \frac{W_{\text{final}}}{W_{\text{initial}}} \right) = k \cdot \ln (35/10) > 0$$

$$\Delta S_{(\text{hot} \rightarrow \text{warm})} = k \cdot \ln \left( \frac{W_{\text{final}}}{W_{\text{initial}}} \right) = k \cdot \ln (35/84) < 0$$
Entropy, Energy, and Temperature

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$\Delta S_{(\text{hot} \rightarrow \text{warm})} = k \cdot \ln \left( \frac{W_{\text{final}}}{W_{\text{initial}}} \right) = k \cdot \ln \left( \frac{35}{84} \right) < 0$

For the overall process, the net entropy change, $\Delta S_{\text{net}}$, is the sum of all the entropy changes involved

$$\Delta S_{\text{net}} = \Delta S_{(\text{cold} \rightarrow \text{warm})} + \Delta S_{(\text{hot} \rightarrow \text{warm})} = k \cdot \ln \left( \frac{35}{10} \right) + k \cdot \ln \left( \frac{35}{84} \right)$$

$$\Delta S_{\text{net}} = k \cdot \ln \left[ \left( \frac{35}{10} \right) \cdot \left( \frac{35}{84} \right) \right] = k \cdot \ln \left( \frac{1225}{840} \right) > 0$$
Entropy, Energy, and Temperature

Consider the entropy change, $\Delta S$, in a process, where $S \equiv k \cdot \ln W$

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$$\Delta S_{\text{net}} = k \cdot \ln \left[ \frac{35}{10} \cdot \frac{35}{84} \right] = k \cdot \ln \left( \frac{1225}{840} \right) > 0$$

Note that the same final result would have been obtained simply by using the values of $W_{\text{total}}$ for the initial and final states.
Entropy, Energy, and Temperature

Questions?
Entropy, Energy, and Temperature

The relationship among entropy, energy (= enthalpy), and temperature.

Consider the entropy changes when 1 quantum of energy is added to our 4-atom model system containing 2 quanta and 1 quantum to another containing 5 quanta.

\[
\Delta S_{(2,4 \rightarrow 3,4)} = k \cdot \ln \left( \frac{W_{3,4}}{W_{2,4}} \right) = k \cdot \ln (\frac{20}{10}) = k \cdot \ln (2.0)
\]

\[
\Delta S_{(5,4 \rightarrow 6,4)} = k \cdot \ln \left( \frac{W_{6,4}}{W_{5,4}} \right) = k \cdot \ln (\frac{84}{56}) = k \cdot \ln (1.5)
\]
Entropy, Energy, and Temperature

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The change in entropy for the cooler system is larger than that for the warmer.
Entropy, Energy, and Temperature

The relationship among entropy, energy (= enthalpy), and temperature. Consider the entropy changes when 1 quantum of energy is added to our 4-atom model system containing 2 quanta and 1 quantum to another containing 5 quanta.

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The change in enthalpy, \( \Delta H \), in each case is the same, +1 quantum.
Entropy, Energy, and Temperature

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The change in entropy for the cooler system is larger than that for the warmer.

The change in enthalpy, \( \Delta H \), in each case is the same, +1 quantum. A relationship that is consistent with these results is

\[ \Delta S = \Delta H / T \]
Entropy, Energy, and Temperature

The relationship among entropy, energy (= enthalpy), and temperature.
Consider the entropy changes when 1 quantum of energy is added to our 4-atom model system containing 2 quanta and 1 quantum to another containing 5 quanta.

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For a given energy (enthalpy) change, the entropy change is larger for a colder body than for a hotter body.
Entropy, Energy, and Temperature

The relationship among entropy, energy (= enthalpy), and temperature. Consider the entropy changes when 1 quantum of energy is added to our 4-atom model system containing 2 quanta and 1 quantum to another containing 5 quanta.

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The change in enthalpy, \( \Delta H \), in each case is the same, +1 quantum. A relationship that is consistent with these results is

\[ \Delta S = \Delta H / T \]

For a given energy (enthalpy) change, the entropy change is larger for a colder body than for a hotter body. The units here are consistent with the definition of \( S \), since the units of the Boltzmann constant, \( k \), are energy per kelvin.
Questions?
Application: Solution Freezing Point
Entropy, Energy, and Temperature

Activity: Gather your two cups of (crushed) ice, 50 mL of water, 50 mL of salt water, a thermometer (or two) and a stout stirrer.
Activity: Gather your two cups of (crushed) ice, 50 mL of water, 50 mL of salt water, a thermometer (or two) and a stout stirrer.

Add water to one cup of ice and salt water to the other. Stir the ice liquid mixtures vigorously while measuring their temperatures and watching Pat do a similar activity.
Activity: Gather your two cups of (crushed) ice, 50 mL of water, 50 mL of salt water, a thermometer (or two) and a stout stirrer.

Add water to one cup of ice and salt water to the other. Stir the ice liquid mixtures vigorously while measuring their temperatures.

What was your result?
   A. $T(\text{ice-water}) = T(\text{ice-salt water})$
   B. $T(\text{ice-water}) > T(\text{ice-salt water})$
   C. $T(\text{ice-water}) < T(\text{ice-salt water})$
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The observations are that the mixture of ice and salt water is at a lower temperature than the ice and pure water mixture.
Entropy, Energy, and Temperature

Consider these changes:
- ice ⇔ water
- ice ⇔ solution (nonvolatile solute)

Quiz: Which of these diagrams represents the relative values of the entropies of ice, water, and solution?
Entropy, Energy, and Temperature

\[ \Delta S_{\text{soln}} > \Delta S_{\text{water}} \]
Entropy, Energy, and Temperature

$\Delta S_{\text{soln}} > \Delta S_{\text{water}}$

$\Delta H_{\text{soln}} = \Delta H_{\text{water}}$ because the change in both cases is ice going to liquid water
Entropy, Energy, and Temperature

\[ \Delta S_{\text{soln}} > \Delta S_{\text{water}} \]

\[ \Delta H_{\text{soln}} = \Delta H_{\text{water}} \] because the change in both cases is ice going to liquid water

Rearrange \( \Delta S = \Delta H/T \) to give \( T = \Delta H/\Delta S \)
Entropy, Energy, and Temperature

\[ \Delta S_{\text{soln}} > \Delta S_{\text{water}} \]

\[ \Delta H_{\text{soln}} = \Delta H_{\text{water}} \] because the change in both cases is ice going to liquid water

Rearrange \( \Delta S = \Delta H/T \) to give \( T = \Delta H/\Delta S \)

For these changes

\[ T_{\text{soln}} = (\Delta H_{\text{soln}})/(\Delta S_{\text{soln}}) < (\Delta H_{\text{water}})/(\Delta S_{\text{water}}) = T_{\text{water}} \]

That is, the temperature at which ice and solution are in equilibrium is lower than the freezing point of water where ice and water are in equilibrium. The freezing point is lowered by nonvolatile solutes.
Entropy, Energy, and Temperature

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Freezing point depression is a colligative property that depends on how much solute is mixed into the solvent, but not on the solute identity.
This result is the basis for using solutes to melt ice on sidewalks in cold climates and for the old fashioned ice-cream makers cooled with ice-salt mixtures.
Entropy, Energy, and Temperature

To check your understanding of the topics in this web seminar, use an entropy-energy-temperature analysis to determine whether the boiling point of an aqueous solution of a nonvolatile solute is higher, lower, or the same as the boiling point of pure water. Model your approach on the one just done for the freezing point of water and an aqueous solution.

See the post-seminar notes that will be posted with the archive for this seminar for the solution.

We welcome your feedback on whether you would like to attend further web seminars exploring more applications of entropy and this model to phase changes, osmosis, chemical reactions, etc. You can do this in the chat here or off-line to me: j_bell@acs.org.
Entropy, Energy, and Temperature

Questions?
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