LIVE INTERACTIVE LEARNING @ YOUR DESKTOP

ACS: ENTROPY: MIXING AND OIL SPILLS

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Familiar Examples of Mixing (and Unmixing)

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Add a water-soluble dye to water.

Quiz: After a long time, what will we observe in the beaker?

A. The dye will coalesce and look similar to the second image above.
B. The dye will spread uniformly throughout the solution.
C. The dye will separate and float on the water.
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B. The dye will spread uniformly throughout the solution.
C. The dye will separate and float on the water.
This was the expected result. Your experience tells you that mixing is a spontaneous process that takes place in one direction, that is, *unmixing of homogeneous mixtures never occurs spontaneously*.

Whatever model we develop to explain mixing, must be consistent with and predict this observation from experience.
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Activity 1: Use your water, oil, and capped bottle.
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Evidently, oil and water separate and do not form a homogeneous mixture. Your experience tells you that this separation is a spontaneous process. Whatever model we develop to explain mixing, must also be consistent with and predict this unmixing observation from experience.
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Let’s pause for Questions?
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The Direction of Change
If a system can exist in more than one observable state (mixed or unmixed, for example), spontaneous changes will be in the direction toward the state that is most probable.
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How do you tell whether two arrangements are distinguishable?
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What is the number of distinguishable arrangements, \( W \), of two identical objects in four boxes where each box can hold only one object? One arrangement is shown below.

Quiz: In the empty two-by-two grid of boxes, stamp two where you could place the objects to form an arrangement that is distinguishable from the one shown.
What is the number of distinguishable arrangements, \( W \), of two identical objects in four boxes where each box can hold only one object?

\[ W = 6. \] The six distinguishable arrangements are:
Let’s pause for Questions?
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A Molecular Mixing Model
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Mixing model: Three dye molecules and 12 water molecules in a 15-cell (3 × 5) container. Initially
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W_{\text{dye}} = 1
\]

Number, \( W_{\text{water}} \), of distinguishable arrangements of water molecules?

\[
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\]

\[
W_{\text{total}} = W_{\text{dye}} \cdot W_{\text{water}} = 1 \cdot 1 = 1
\]
Now allow the dye molecules to begin to mix into the water, so they can occupy any of the cells in the top two layers, that is three identical molecules and six possible cells. One possible arrangement is

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

$$W_{n,N} = \frac{N!}{n!(N-n)!}.$$
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$$W_{\text{dye}} = W_{3,6} = \frac{6!}{3!(6-3)!} = \frac{6 \cdot 5 \cdot 4 \cdot (3!)}{(3 \cdot 2 \cdot 1) \cdot (3!)} = \frac{6 \cdot 5 \cdot 4}{3 \cdot 2 \cdot 1} = \frac{120}{6} = 20$$
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$W_{\text{water}} = 1$ (only one choice for waters, once dye locations chosen)

$W_{\text{total}} = W_{\text{dye}} \cdot W_{\text{water}} = 20 \cdot 1 = 20$
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Continuing the mixing successively into 9, 12, and all 15 cells gives
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Quiz:
As a check on what we have done, look at the system from the point of view of the water molecules. Use the formula you have to calculate $W_{12,15}$, that is, the number of ways of arranging 12 objects (water molecules) in 15 cells. Enter your result.

A. $W_{12,15} < 455$      B. $W_{12,15} = 455$      C. $W_{12,15} > 455$
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A. $W_{12,15} < 455$  
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The calculation and result are

$$W_{12,15} = \frac{15!}{12!(15-12)!} = \frac{15 \cdot 14 \cdot 13 \cdot (12!)}{12!(3 \cdot 2 \cdot 1)} = \frac{15 \cdot 14 \cdot 13}{(3 \cdot 2 \cdot 1)} = \frac{5 \cdot 7 \cdot 13}{1} = 455 = W_{\text{water}}$$

$$W_{\text{total}} = W_{\text{dye}} \cdot W_{\text{water}} = 1 \cdot 455 = 455$$
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Continuing the mixing successively into 9, 12, and all 15 cells gives

If a system can exist in more than one observable state spontaneous changes will be in the direction toward the state that is most probable. Our model shows what you know:

mixing is a spontaneous process
Let’s pause for Questions?
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Probability and Entropy
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**ENTROPY (S)**

Definition (molecular viewpoint) \( S \equiv k \cdot \ln W \)

\( k \) is Boltzmann’s constant
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Note that the combination of numbers of arrangements, \( W_s \), is multiplicative, as demanded by the rules of combinations and permutations.

However, we want thermodynamic functions to be additive and the logarithmic dependence of \( S \) on \( W \), makes entropies for different parts of a system additive. For example:

\[
S_{\text{total}} = k \cdot \ln W_{\text{total}} = k \cdot \ln(W_{\text{dye}} \cdot W_{\text{water}}) = k \cdot \ln W_{\text{dye}} + k \cdot \ln W_{\text{water}} = S_{\text{dye}} + S_{\text{water}}
\]
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ENTROPY (S)

Definition (molecular viewpoint) \[ S \equiv k \cdot \ln W \]
\[ k \] is Boltzmann’s constant

Consider a change for which the total number of arrangements increases, that is \[ W_{\text{final}} > W_{\text{initial}} \], a spontaneous change.

For this change:

\[ \Delta S_{\text{total}} = k \cdot \ln W_{\text{final}} - k \cdot \ln W_{\text{initial}} = k \cdot \ln \left( \frac{W_{\text{final}}}{W_{\text{water}}} \right) > 0 \]
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Entropy increases in spontaneous changes
Note that another, more fundamental, way to view the increasing entropy as mixing occurs in our model is that the volume available for the molecules (dye or water) to mix into is increasing. Thus, the larger the volume a system of molecules can occupy, the higher the entropy.
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Entropy, Oil, and Water
Why don’t oil and water mix? Water molecules surround non-polar solutes and are “frozen out” (dark blue) of the rest of the liquid, thus reducing the effective volume available to the solvent molecules.

“Free” water = 39 – 12 = 27
“Free” water = 39 – 7 = 32

$S_{mix} < S_{unmix}$
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Why don’t oil and water mix? Spontaneous process is unmixing. Oil spills float on the surface--as you observed previously.
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One way to ameliorate an oil spill is to add “dispersants,” which are detergents, ambiphilic molecules with polar and nonpolar ends.
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entropy increases

micelle formation
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One way to ameliorate an oil spill is to add “dispersants,” which are detergents, ambiphilic molecules with polar and nonpolar ends.
Activity 2: Add detergent to your oil and water mixture, cap the bottle, and shake well. Also watch as Pat adds an egg yolk to her vinegar and oil dressing. Observe and record what happens to your mixture.
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The phospholipids and proteins in an egg yolk are ambiphilic molecules that act like your detergent molecules to disperse the oil in the vinegar to form a stable emulsion. With the appropriate recipe, this is how we make mayonnaise.
Different conditions may yield different results. High pressure of small non-polar molecules and low temperature to encourage formation of a solid water phase can produce this change.

\[ S_{\text{unmix}} < S_{\text{mix}} \]

Little freedom of movement

Solutes mix into many cells
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Mixing, formation of clathrates, gas hydrates -- non-polar molecules in the relatively open structure of some forms of ice, is spontaneous. As methane at high pressure seeps out of fissures into cold water at the bottom of the sea (Gulf of Mexico, for example), clathrate formation is rapid.

So rapid, that the gushing methane gas from the Gulf oil spill formed the clathrate immediately and clogged a container designed to trap the oil.
Note that temperature is a factor in the formation of clathrates, but we have not yet connected entropy and temperature. That is our task in the next ACS-NSTA web seminar.

December 15, 2010

*Entropy, Energy, and Temperature*
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