Entropy of mixing

The meaning of entropy: Entropy of mixing

Consider that a number of ideal gases are separated which
are present in a vessel. Let n_i be the number of moles
of each gas and V_i is the volume it occupies. The total entropy,

$$S_1 = \sum n_i (C_v \ln T + R \ln V_i + S_i) \quad 1$$

Note the term S_i. It is because,

$$dS = C_v(dT/T) + R(dV/V)$$
$$S = C_v \ln T + R \ln V + S_0$$

Let the partitions between the gases are removed and they are
allowed to mix. Let the volume the gases occupy is V. The entropy,

$$S_2 = \sum n_i (C_v \ln T + R \ln V + S_i) \quad 2$$

Assume that the pressure has not changed and there is no change in temperature.

Ratio of volume,

$$V_i/V = n_i/n = X_i \; - \; \text{the mole fraction.}$$

Where n is the total number of moles.

Substituting $V_i = VX_i$ in Eqn.1

$$S_1 = \sum n_i \, (C_v \ln T + R \ln V + R \ln X_i + S_i)$$

The increase in entropy, the entropy of mixing,

$$S_2 - S_1 = -\sum n_i \, R \ln X_i$$

Entropy of mixing of 1 mole of the ideal gas,

$$\Delta S_m = - R \sum n_i/n \ln X_i = -R \sum X_i \ln X_i$$

The fraction X_i is less than unity in all cases, the logarithm is negative and thus ΔS_m is always positive.

Thus mixing of gases (eg. by diffusion), always results in increase in entropy. **Mixing is spontaneous!**

This is in general true of any material, liquid or solid.

Entropy and disorder

Spontaneous processes → net increase in entropy → increase in randomness of distribution (mixing).

The diffusion of initially separated gases
result in an increase in entropy. The process has
increased the random distribution of molecules. Spontaneous
conduction of heat results in the random distribution of kinetic energy
of the atoms. Thus spontaneous processes increase randomness,
at the same time increases entropy. Therefore, it is appropriate to
suggest a relationship between

entropy and randomness.

This definition of entropy, that it is a measure of randomness, is one of great value. Apart form the quantitative relationship, the concept is of great value in understanding chemical processes quantitatively. A measure of entropy changes gives an indication of structural changes. The process of fusion involves increase in disorder and therefore, the entropy increase. Greater the disorder, greater the entropy increase. Therefore, the heat of fusion of ice and benzene are 5.26 and 8.27 cal/deg/mol. The difference is because in water there is considerable amount of order due to hydrogen bonding while there is no such interaction in benzene.

Entropy and probability

A correlation is possible between entropy and probability.

Suppose there are two bulbs, connected through a valve, and assume that one bulb is evacuated and the other is full of gas. As the stopcock is opened, according to second law, the gas will distribute uniformly.

We can explain this using the theory of probability.

Assume that there is just one molecule in the system. Here, the probability that it can be found in one bulb is ½ , ie. one chance in two.
 If we have 2 molecules, the probability that two will be found in one bulb is ¼ ie. $(½)^2$. If there are N molecules, the probability that all the molecules will be found in one bulb is $(½)^N$. For a bulb having one litre volume and the pressure is one atmosphere, the number of molecules is 10^{22}.

Even for 10^{-6} atm, the number of molecules is 10^{16}.
Thus the probability for the molecules to reside in one bulb is very small. This is also the probability for the molecules to return to one bulb after being distributed uniformly.

Thus it can be considered that the spontaneous process in which the gas is distributed uniformly in two bulbs is associated with the large probability. All spontaneous processes represent changes from a less portable state to a more portable state.

Since processes are accompanied by increase in entropy it is possible that there is a relation between entropy and probability.

If S is the entropy and W is the probability, $S = f(W)$

If there are two systems of probability, W_A and W_B, with entropies S_A and S_B, the combined system will have entropy $S_A + S_B$ and probability $W_A \times W_B$.
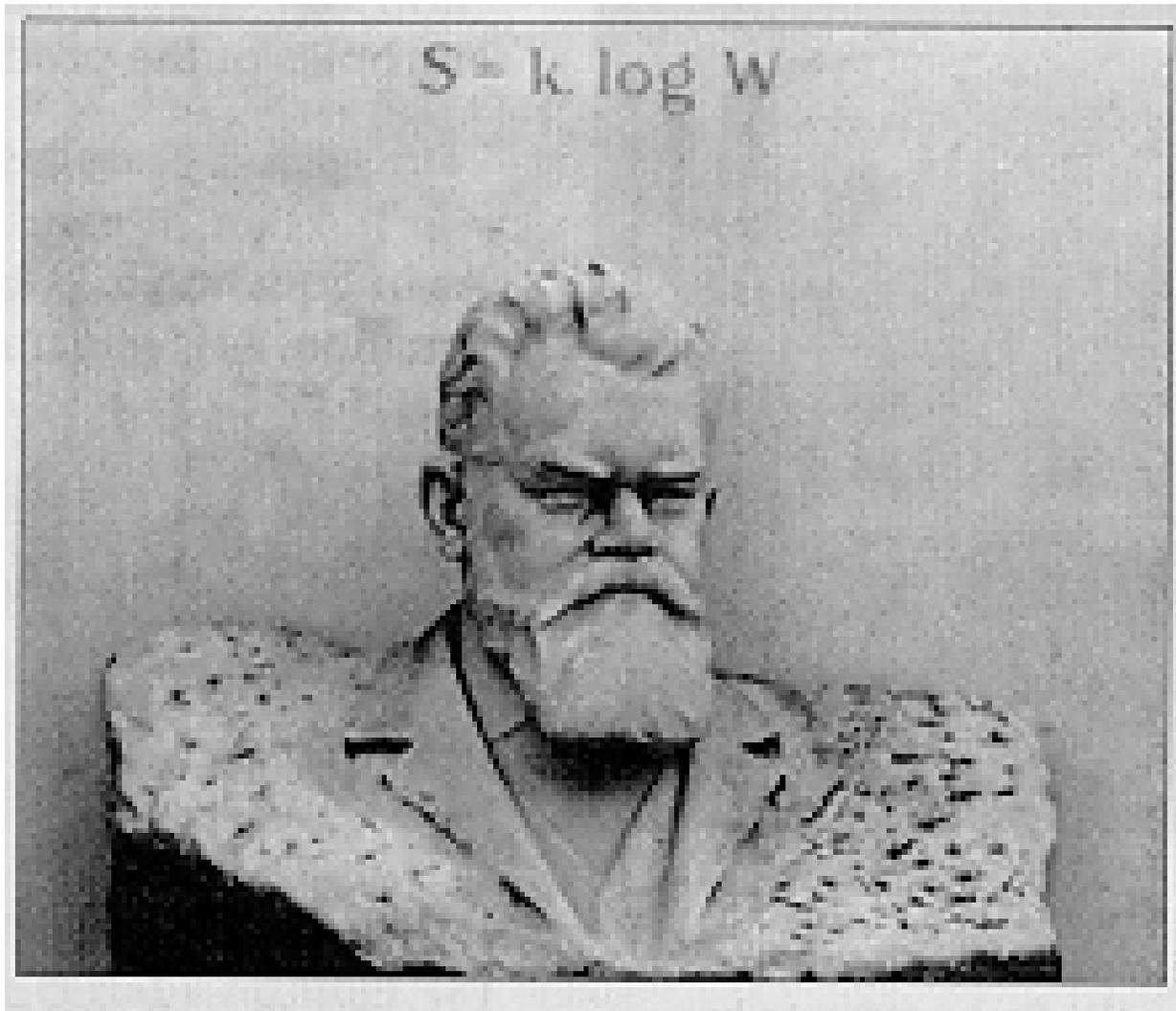
$$S_{AB} = S_A + S_B = f(W_A \times W_B)$$
$$f(W_A) + f(W_B) = f(W_A \times W_B)$$
Thus the function has to be logarithmic.
$$S = k \ln W + \text{constant}$$

Where k is the Botzmann constant, R/N. It has been shown later that the constant is zero and $S = k \ln W$.

There is no complete proof for this expression and therefore has to be regarded as a postulate.   Now the task to calculate entropy is to determine probability.

Use of statistical mechanics.

Tombstone of Ludwig Boltzmann

Boltzmann paradox and a discussion on entropy and probability

Let us assume that we have a small box in a room containing some gas. Assume that the walls of the box are made open and the gas was free to mix. Sometime later the gas spread uniformly in the box.

For each of the molecule originally in the box, the probability of one motion is just the same as the motion in the opposite direction. So why is that the reverse of the process, namely the opposite of random diffusion, is not observed? The fact that some motions of a system are never observed is called Boltzmann paradox.

The puzzle is solved by looking at the following fact. The probability of motion for one molecule is just the same as the reverse motion. However, the probability of a group of molecules for uniform filling of available space is enormously greater than the probability for occupation in one part of the box.

Assume that we have two balls and two cells. There is only one way
to fill the cells uniformly, so probability of uniform filling is one. Let us say we
have four cells and two balls. After two cells, there is a partition.
Consider various kinds of arrangements. We see that there are two
kinds of non uniform filling possibilities and four kinds of uniform
filling possibilities. So we see that probability of uniform filling is, 4/6.
The probability of finding two balls in one side of the box is 2/6 or 1/3.

Four cells

Two balls and two cells
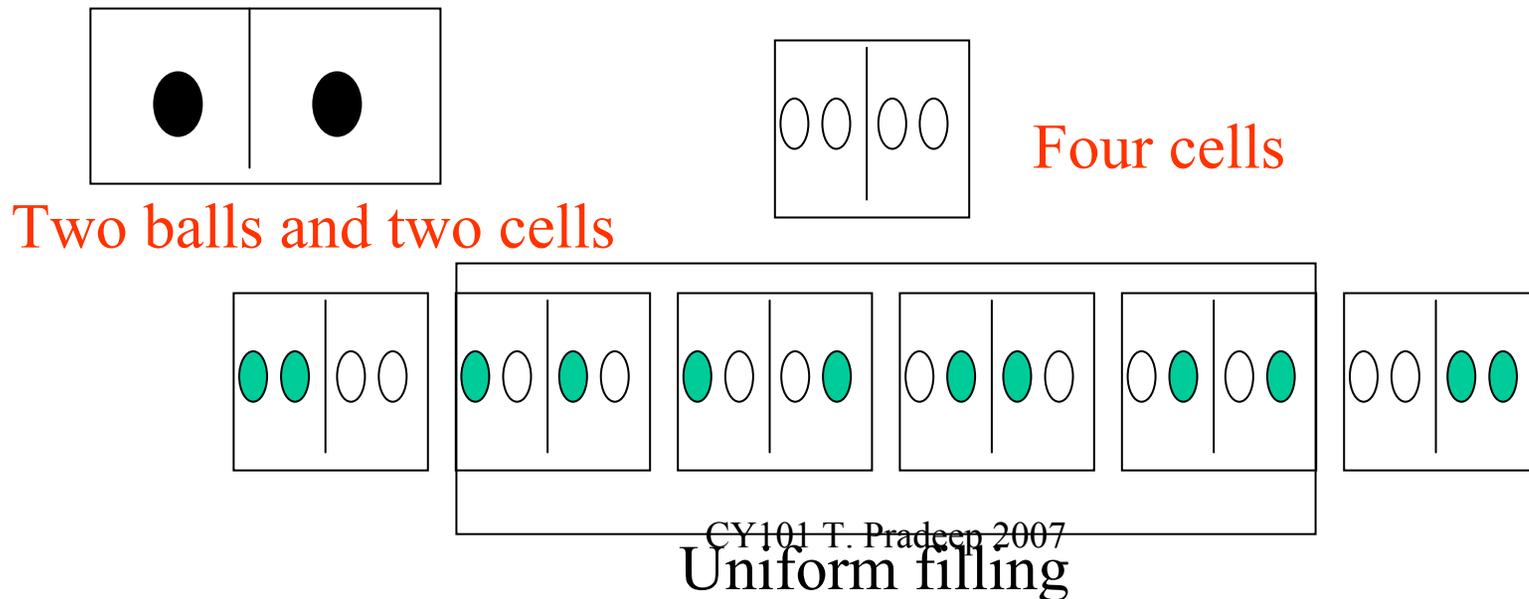
Uniform filling

Now let us say we have eight cells. There are 28 arrangements and 16 of them correspond to uniform filling. Thus probability of uniform filling is 16/28 or 4/7. Now one can see that as the number of cells increase, the probability of uniform filling approaches ½.

The entropy of the system is related to the number of arrangements of particles of the system, called the **complexion**, Ω of the system.

The Boltzmann definition of entropy, $S = k \ln \Omega$

For two balls in one box, $S_1 = k \ln \Omega = k \ln (1) = 0$

For the six arrangements, $S_2 = k \ln 6$

The entropy difference upon expansion from 2 cells to six cells,

$\Delta S = S_2 - S_1 = k \ln 6$ for 2 balls
$= \frac{1}{2} k \ln 6$ for 1 ball

How about N cells?

For the first ball, there are N possibilities. For the second, there are N-1 possibilities. Thus there are N (N-1) possibilities. Since we cannot distinguish between the two balls, we will have to take the total number of distinct arrangements as, N(N-1)/2.

So, entropy for this arrangement, S_1 = k ln [N(N-1)/2]
For N′ cells,

S_2 = k ln [N′(N′-1)/2]
$\Delta S = S_2 - S_1$ = k ln {N′(N′-1)/N(N-1)}

Let us say N is very large. Then N and N-1 are the same.
$\Delta S = S_2 - S_1$ = k ln (N′/N)^2 = 2k ln (N′/N)

For ideal gases, the number of cells correspond to volume,

$\Delta S = 2k \ln (V'/V)$ for two molecules,

$\Delta S = k \ln (V'/V)$ for one molecule.

$\Delta S = R \ln (V'/V)$ for one mole.

This is what we got for the expansion of one mole of ideal gas.