

# Lecture 5

## Entropy and Disorder

## Third law

$$S(T) = S(0) + C_p \ln T$$

Background information:  $\int_1^2 dS = n C_p \ln T_2/T_1 - nR \ln P_2/P_1$

The change in entropy can be calculated using graphical method.

In all these cases, the only parameter which is impossible to measure is  $S(0)$ . This parameter has to be evaluated for determining the value of  $S(T)$

[note: absolute entropy, not  $\Delta S$ ]. Here comes third law of thermodynamics.

“Value of  $S(0)$  is zero for every pure, perfectly crystalline substance”

M. Plank, 1913

Then,  $S(T) = C_p \ln T$

$S(T)$  is called the third law entropy,  $S_T$  or simply entropy at temperature  $T$  and pressure  $P$ .

If pressure is 1 atm, it is called standard entropy,  $S^0_T$

To measure  $S(T)$ , we need to measure  $C_p$  as a function of  $T$ .

Measuring  $C_p$  down to absolute zero is not done as  $C_p$  obeys Debye law,  $C_p = aT^3$ ,  $a$  is a constant for a material.

So  $C_p$  is measured up to a temperature,  $T'$  and  $S(T)$  is calculated from,

$$\int_{T'}^T C_p/T dT = \int_{T'}^T C_p d(\ln T) = 2.303 \int_{T'}^T C_p d(\ln T)$$

Is evaluated graphically. These numbers are tabulated.

# Absolute entropy: evaluation

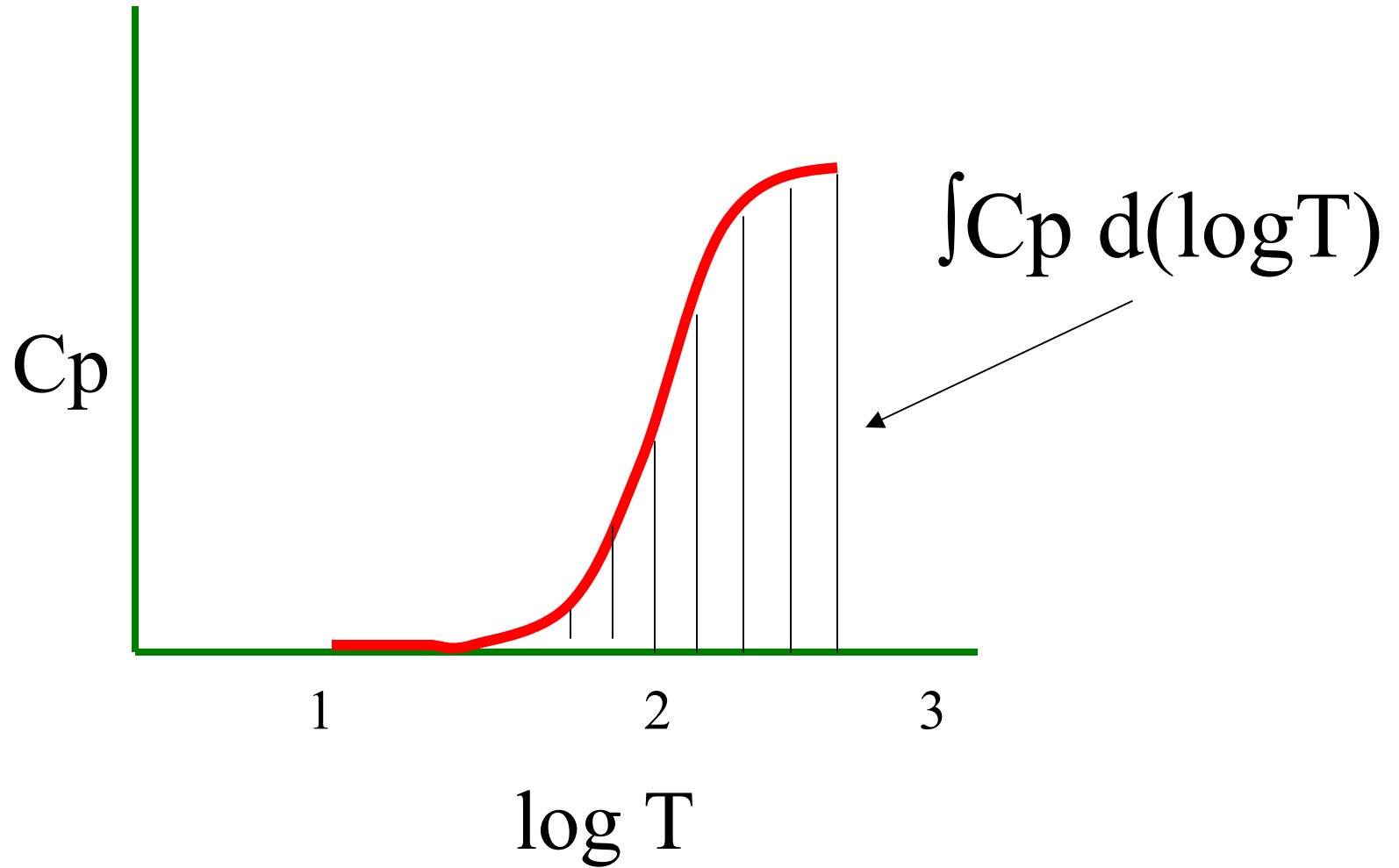


Table 9.1  
Standard entropies at 298.15 K

Substance	$S_{298.15}^{\circ}/R$	Substance	$S_{298.15}^{\circ}/R$
<b>Solids</b>		<b>Liquids</b>	
<i>Single unit, simple</i>		Hg	9.129
C (diamond)	0.286	Br <sub>2</sub>	18.3068
Si	2.262	H <sub>2</sub> O	8.4131
Sn (white)	6.156	TiCl <sub>4</sub>	30.55
Pb	7.79	CH <sub>3</sub> OH	15.2
Cu	3.987	C <sub>2</sub> H <sub>5</sub> OH	19.3
Fe	3.28		
Al	3.410	<b>Gases</b>	
Ca	5.00	<i>Monatomic</i>	
Na	6.170	He	15.1591
K	7.779	Ne	17.5856
<i>Single unit, complex</i>		Ar	18.6101
I <sub>2</sub>	13.968	Kr	19.7213
P <sub>4</sub>	19.77	Xe	20.3951
S <sub>8</sub> (rhombic)	30.842	<i>Diatomic</i>	
C (graphite)	0.690	H <sub>2</sub>	15.7041
<i>Two unit, simple</i>		HF	20.8872
SnO	6.876	HCl	22.4653
PbS	11.0	HBr	23.8844
HgO(red)	8.449	HI	24.8340
AgCl	11.57	Cl <sub>2</sub>	26.8167
FeO(wustite)	6.91	O <sub>2</sub>	24.6604
MgO	3.241	N <sub>2</sub>	23.0325
CaO	4.58	NO	25.336
NaCl	8.68	CO	23.7607
KCl	9.93	<i>Triatomic</i>	
KBr	11.53	H <sub>2</sub> O	22.6984
KI	12.79	O <sub>3</sub>	28.72
<i>Two unit, complex</i>		NO <sub>2</sub>	28.86
FeS <sub>2</sub> (pyrite)	6.37	N <sub>2</sub> O	26.43
NH <sub>4</sub> Cl	11.4	CO <sub>2</sub>	25.6996
CaCO <sub>3</sub> (calcite)	11.2	<i>Tetatomic</i>	
NaNO <sub>3</sub>	14.01	SO <sub>3</sub>	30.87
KClO <sub>3</sub>	17.2	NH <sub>3</sub>	23.173
<i>Three units, simple</i>		P <sub>4</sub>	33.66
SiO <sub>2</sub> ( $\alpha$ -quartz)	4.987	PCl <sub>3</sub>	37.49
Cu <sub>2</sub> O	1.20	C <sub>2</sub> H <sub>2</sub>	24.15
Ag <sub>2</sub> O	4.6	<i>Pentatomic</i>	
Na <sub>2</sub> O	9.03	CH <sub>4</sub>	22.389
<i>Five units, simple</i>		SiH <sub>4</sub>	24.60
Fe <sub>2</sub> O <sub>3</sub>	10.51	SiF <sub>4</sub>	33.995

Calculated from values in NBS Technical Notes 270-3 through 270-8. U.S. Government Printing Office, 1968-81; and in No. 28 CODATA Recommended Values for Thermodynamics 1977. (April 1978) International Council of Scientific Unions.

## Nernst heat theorem

The Nernst heat theorem states that, “the entropy change accompanying a physical or chemical change approaches zero as temperature tends to zero.  $\Delta S \rightarrow 0$  as  $T \rightarrow 0$ ”.

This form of third law is less restrictive than the Plank’s statement.

## Another form:

“If entropy of every element at absolute zero in their standard state is taken to be zero, all substances have positive entropy which may become zero at  $T = 0$  and it will indeed become zero for all perfectly crystalline solids.”

For a non-crystalline state, the entropy could become nonzero as the first part of the statement reads.

# Entropy change

For a reaction, standard entropy is defined just as we define standard enthalpy.

$$\Delta_{\text{reaction}} S = \sum S_{\text{products}} - \sum S_{\text{reactants}}$$

$$\begin{aligned} (\partial \Delta S^0 / \partial T)_P &= (\partial S_{\text{products}} / \partial T)_P - (\partial S_{\text{reactants}} / \partial T)_P \\ &= C_{P, \text{Products}}^0 / T - C_{P, \text{Reactants}}^0 / T = \Delta C_P^0 / T \end{aligned}$$

This equation can be written in differential form can be integrated.

$$\int_{T_0}^T d(\Delta S^0) = \int_{T_0}^T \Delta C_P^0 / T dT$$

$$\Delta S_T^0 = \Delta S_{T_0}^0 + \int_{T_0}^T \Delta C_P^0 / T dT$$



# How do you reach low temperature?

Adiabatic demagnetization

Adiabatic nuclear demagnetization

Laser cooling

## 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,

$$V_i/V = n_i/n = N_i$$

Where  $n$  is the total number of moles.

Substituting  $V_i = VN_i$  in Eqn.1

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

The increase in entropy, the entropy of mixing,

$$S_2 - S_1 = -\sum n_i R \ln N_i$$

Entropy of mixing of 1 mole of the ideal gas,

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

The fraction  $N_i$  is less than unity in all cases, the logarithm is negative and thus  $\Delta S_m$  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  $\rightarrow$  net increase in entropy  $\rightarrow$  increase in randomness of distribution.

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 from 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  $\frac{1}{2}$  ie. one chance in two.

If we have 2 molecules, the probability that two will be found in one bulb is  $\frac{1}{4}$  ie.  $(\frac{1}{2})^2$ . If there are N molecules, the probability that all the molecules will be found in one bulb is  $(\frac{1}{2})^N$ . 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.

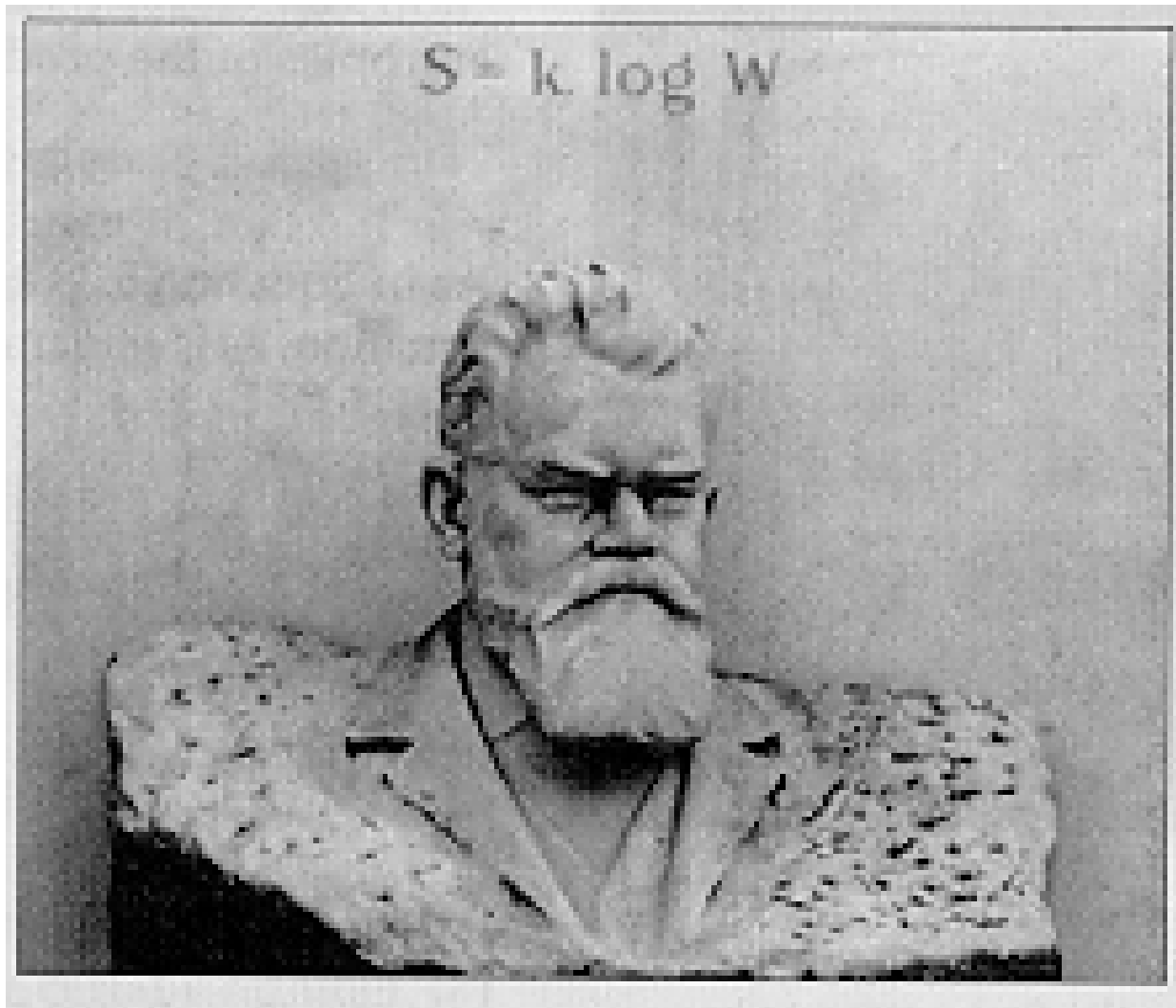
$$S = k \ln W + \text{constant}$$

Where  $k$  is the Boltzmann 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**

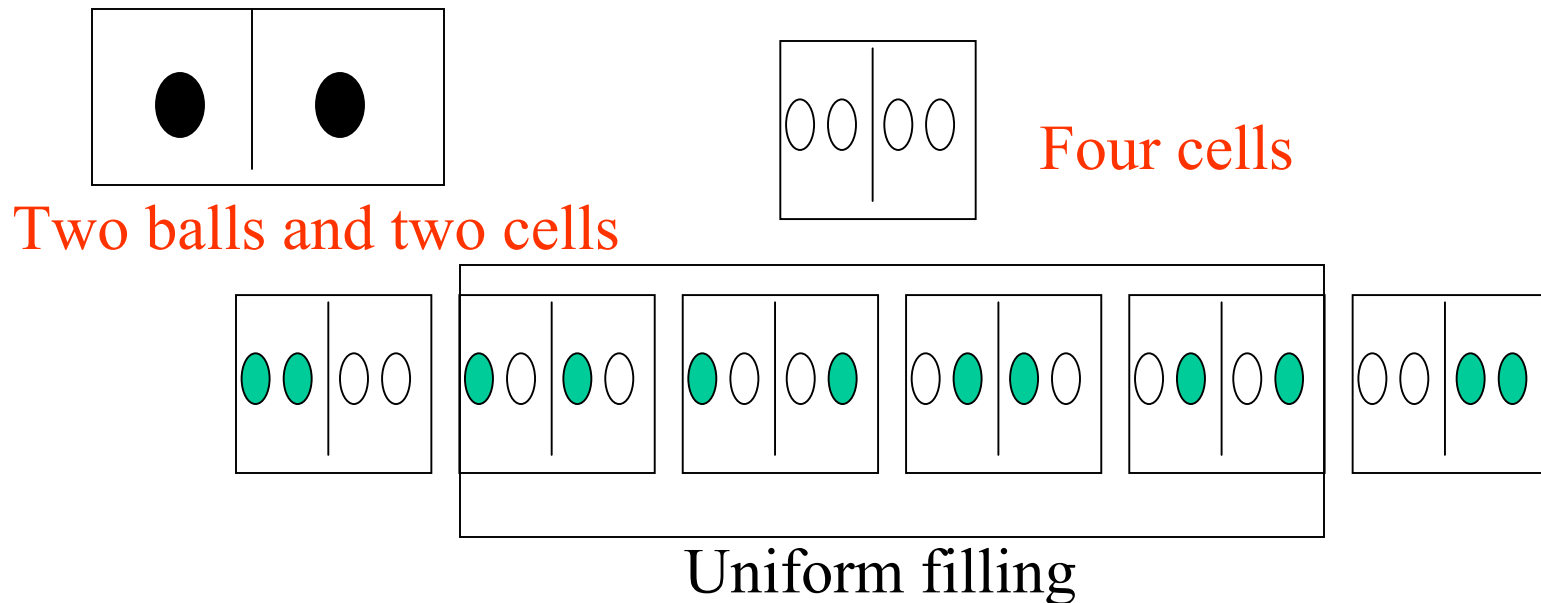
# Boltzmann paradox and a discussion on entropy and probability

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  $1/3$ .



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  $1/2$ .

The entropy of the system is related to the number of arrangements of particles of the system, called the **complexion**,  $\Omega$  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,

$$\begin{aligned} \Delta S = S_2 - S_1 &= k \ln 6 \text{ for 2 balls} \\ &= \frac{1}{2} k \ln 6 \text{ for 1 ball} \end{aligned}$$

## 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.