

## Chemistry 331

### Lecture 10 Second Law Applications

NC State University

## Summary of entropy calculations

In the last lecture we derived formula for the calculation of the entropy change as a function of temperature and volume changes. These are summarized in the table below.

Constant temperature	$\Delta S = nR \ln(V_2/V_1)$
Constant volume	$\Delta S = nC_v \ln(T_2/T_1)$
Constant pressure	$\Delta S = nC_p \ln(T_2/T_1)$

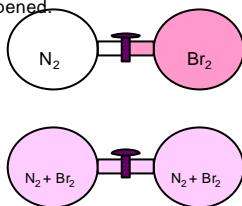
Sometimes we only have pressure information and the entropy change can be rewritten as follows.

$$P_1 V_1 = P_2 V_2 \Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right)$$

## Entropy of mixing

When two substances can mix there is a spontaneous tendency for this occur. We quantify this using the entropy state function. If we consider two containers separated by a stopcock. It  $N_2$  gas is in one and  $Br_2$  gas is in the other we know from experience that the gases will mix once the stopcock is opened.



## Entropy of mixing

For each gas we can describe the mixing as a volume change. The  $N_2$  gas is originally on the right side contained in volume  $V$  at pressure  $P$ . After opening the stopcock, the available volume is  $2V$  and the partial pressure of  $P_1 = x_1 P$ . The same is true for  $Br_2$ . Its initial pressure is  $P_2$  and final pressure is  $P_2 = x_2 P$ . We treat the entropy as the sum of two expansions (i.e. an expansion for each gas).

$$\Delta_{mix} S = \Delta_{exp} S_1 + \Delta_{exp} S_2$$

$$\Delta_{mix} S = -n_1 R \ln\left(\frac{P_1}{P}\right) - n_2 R \ln\left(\frac{P_2}{P}\right)$$

$$\Delta_{mix} S = -n_1 R \ln(x_1) - n_2 R \ln(x_2)$$

$$\Delta_{mix} S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

Note that the mole fraction applies to the final composition

## Entropy of phase transition

The entropy of phase transition can be calculated using the enthalpy and temperature of the transition.

$$\Delta_{fus} S = \frac{q_{P,fus}}{T_{fus}} = \frac{\Delta_{fus} H}{T_{fus}}$$

Example, using the data in the Table calculate the entropy of vaporization for the following compounds.

Compound	$\Delta_{vap} H$ kJ/mol	$T_b$ K
$C_2H_6$	30.8	353.2
$C_2H_5$	14.7	184.6
$CCl_4$	30.0	350.0
$CH_4$	8.18	111.7
$Br_2$	29.7	332.4
$H_2S$	18.7	212.8

Solution: Use the following relation

$$\Delta_{vap} S = \frac{\Delta_{vap} H}{T_{vap}}$$

## Entropy of phase transition

The entropy of phase transition can be calculated using the enthalpy and temperature of the transition.

$$\Delta_{fus} S = \frac{q_{P,fus}}{T_{fus}} = \frac{\Delta_{fus} H}{T_{fus}}$$

Example, using the data in the Table calculate the entropy of vaporization for the following compounds.

Compound	$\Delta_{vap} H$ kJ/mol	$T_b$ K	$\Delta_{vap} S$ J/mol-K
$C_2H_6$	30.8	353.2	87.2
$C_2H_5$	14.7	184.6	79.6
$CCl_4$	30.0	350.0	85.7
$CH_4$	8.18	111.7	73.2
$Br_2$	29.5	332.4	88.5
$H_2S$	18.7	212.8	87.7

Note the similarity in the values for the entropy of vaporization. This is known as Trouton's rule.

## Conformational entropy

The entropy of a polymer or a protein depends on the number of possible conformations. This concept was realized first more than 100 years ago by Boltzmann. The entropy is proportional to the natural logarithm of the number of possible conformations,  $W$ .

$$S = R \ln W$$

For a polymer  $W = M^N$  where  $M$  is the number of possible conformations per monomer and  $N$  is the number of monomers. For a typical polypeptide chain in the unfolded state  $M$  could be a number like 6 where the conformations include different  $\phi, \psi$  angles and side chain angles. On the other hand, when the protein is folded the conformational entropy is reduced to  $W = 1$  in the theoretical limit of a uniquely folded structure. Thus, we can use statistical considerations to estimate the entropy barrier to protein folding.

## Problem solving

We can identify the following main types of problems that involve entropy change:

- Isothermal expansion/compression (reversible/irreversible)
- Temperature change
- Equilibration
- Mixing
- Phase Transition
- Statistical or Conformational Entropy
- Adiabatic (trick question) if  $q = 0$  then  $\Delta S = 0$ .

Whenever you are solving an entropy problem remember to consider both system and surroundings. The system is always calculated along a reversible path.

## Isothermal compression

Calculate the entropy for an irreversible compression of oxygen gas. The initial pressure of the gas is 1 bar in a volume of 100 L. The final pressure of the gas is 10 bar and the temperature is 400 K.

**Solution:** Note that you need to obtain the number of moles. The problem does not ask you for a molar entropy. Write down the expression for the entropy:

$$\Delta S = nR \ln \left( \frac{V_2}{V_1} \right) = nR \ln \left( \frac{P_1}{P_2} \right)$$

We need either the ratio of volumes or the ratio of pressures. We are given the pressures so we can use those.  
 $P_2/P_1 = 10 \text{ bar} / 1 \text{ bar} = 10$ .

## Isothermal compression

We obtain the number of moles using the ideal gas law:

$$\begin{aligned} n &= \frac{P_1 V_1}{RT} = \frac{(10^5 \text{ Pa})(0.1 \text{ m}^3)}{(8.31 \text{ J mol}^{-1} \text{ K})(400 \text{ K})} \\ &= \frac{(1 \text{ bar})(100 \text{ L})}{(0.0831 \text{ L-bar/mol-K})400 \text{ K}} \\ &= 3.00 \text{ moles} \end{aligned}$$

Now we can substitute into the entropy expression:

$$\Delta S = nR \ln \left( \frac{P_1}{P_2} \right) = (3.0 \text{ mol})(8.31 \text{ J/mol-K}) \ln(10) = 249 \text{ J/K}$$

## Equilibration

We have seen a simple example where there are two metal blocks, both made of the same material. However, this need not be the case. For any arbitrary materials 1 and 2 in contact we need to know the initial temperatures and heat capacities to calculate the final temperature.

$$q_1 = -q_2$$

$$C_{p,1}(T_1 - T_{eq}) = -C_{p,2}(T_2 - T_{eq})$$

Now we solve for the equilibrium temperature  $T_{eq}$ .

$$C_{p,1}T_1 - C_{p,1}T_{eq} = -C_{p,2}T_2 + C_{p,2}T_{eq}$$

$$C_{p,1}T_1 + C_{p,2}T_2 = (C_{p,1} + C_{p,2})T_{eq}$$

$$T_{eq} = \frac{C_{p,1}T_1 + C_{p,2}T_2}{C_{p,1} + C_{p,2}}$$

## Equilibration: Calculating the entropy

Once you have obtained the equilibrium temperature, the entropy is easily calculated from:

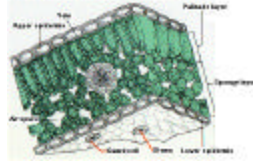
$$\Delta S_1 = nC_{p,1} \ln \left( \frac{T_{eq}}{T_1} \right), \Delta S_2 = nC_{p,2} \ln \left( \frac{T_{eq}}{T_2} \right)$$

In such problems, you are assuming that the two objects in thermal contact are a closed system. The overall entropy for heat flow should be positive since heat flow from a hotter to a colder body is a spontaneous process.

**Example:** The coffee cup problem. A hiker uses an aluminum coffee cup. If the mass of the cup is 4 grams and the ambient temperature (i.e. the cup's temperature) is  $-10^\circ\text{C}$  and the hiker pours 50 ml. of coffee with a temperature of  $90^\circ\text{C}$  into the cup:  
 A. Calculate the equilibrium temperature.  
 B. Calculate the entropy change.

## Gas exchange in a green leaf

The cells of the spongy layer are irregular in shape and loosely packed. Their main function seems to be the temporary storage of sugars and amino acids synthesized



in the palisade layer. They also aid in the exchange of gases between the leaf and the environment. During the day, these cells give off oxygen and water vapor to the air spaces that surround them. They also pick up carbon dioxide from the air spaces. The air spaces are interconnected and open to the outside through pores called stomata (singular, stoma).

## Entropy O<sub>2</sub> mixing in a the stomata of a leaf

During photosynthesis O<sub>2</sub> is produced in the thylakoid membrane of green leaves. The gas meets the atmosphere in the stomata of the leaf. Assuming that the following mole fractions exist calculate the molar entropy of mixing.

Inside  $x_{O_2, in} = 0.5$  and  $x_{N_2, in} = 0.5$

Outside  $x_{O_2, out} = 0.2$  and  $x_{N_2, out} = 0.8$

Assume that the stomata closes with an equal volume of outside air and inside gas present in an enclosed space.

**Solution:** Assume that the initial state is premixed gas both inside and outside. Call oxygen compound 1 and nitrogen compound 2. The final composition is:

$$x_{O_2} = (x_{O_2, in} + x_{O_2, out})/2 = (0.5 + 0.2)/2 = 0.35$$

$$x_{N_2} = (x_{N_2, in} + x_{N_2, out})/2 = (0.5 + 0.8)/2 = 0.65$$

## Entropy O<sub>2</sub> mixing in a the stomata of a leaf

Write down the total entropy change as products (final mixed composition) minus reactants (premixed air from inside and outside). There is an entropy of mixing of each of the two "reactants" that must be subtracted from the entropy of the final mix. Note that there is half as much of each of the reactant gases as the product.

$$\begin{aligned} \Delta S_{total} &= \Delta S_{final\_mix} - \Delta S_{mix\_in} - \Delta S_{mix\_out} \\ &= -nR \left\{ x_{O_2} \ln x_{O_2} + x_{N_2} \ln x_{N_2} \right\} \\ &\quad + \frac{nR}{2} \left\{ x_{O_2, in} \ln x_{O_2, in} + x_{N_2, in} \ln x_{N_2, in} \right\} \\ &\quad + \frac{nR}{2} \left\{ x_{O_2, out} \ln x_{O_2, out} + x_{N_2, out} \ln x_{N_2, out} \right\} \end{aligned}$$

Since the problem asks for the molar entropy we really need  $\Delta S_{final\_mix}/n$  so we can write the formula as:

## Entropy O<sub>2</sub> mixing in a the stomata of a leaf

Write down the total entropy change as products (final mixed composition) minus reactants (premixed air from inside and outside). There is an entropy of mixing of each of the two "reactants" that must be subtracted from the entropy of the final mix. Note that there is half as much of each of the reactant gases as the product.

$$\begin{aligned} \Delta S_{total, m} &= -R \left\{ x_{O_2} \ln x_{O_2} + x_{N_2} \ln x_{N_2} - \frac{x_{O_2, in}}{2} \ln x_{O_2, in} - \frac{x_{N_2, in}}{2} \ln x_{N_2, in} - \frac{x_{O_2, out}}{2} \ln x_{O_2, out} - \frac{x_{N_2, out}}{2} \ln x_{N_2, out} \right\} \\ &= (8.31 \text{ J/mol-K})(0.05) = 0.421 \text{ J/mol-K} \end{aligned}$$

This is a small entropy. Part of the reason is that the gases were already mixed. If they had been completely unmixed the entropy would have been ~ 5.4 J/mol-K.

## Phase Transition

Compare the entropy of sublimation of water to the entropy of vaporization at 0°C. Which is larger? Why?

**Solution:** The entropy of a phase transition is given by:

$$\Delta S_{phase} = \frac{\Delta H_{phase}}{T_{phase}}$$

From the information in Atkins (page 61) we find that  $\Delta_{vap}H = 45.07 \text{ kJ/mol}$  and  $\Delta_{sub}H = 51.08 \text{ kJ/mol}$ . Using these values and the temperature of 273 K we find.

$$\Delta S_{vap} = \frac{45070 \text{ J/mol}}{273 \text{ K}} = 165.1 \text{ J/mol-K}$$

$$\Delta S_{sub} = \frac{51080 \text{ J/mol}}{273 \text{ K}} = 187.1 \text{ J/mol-K}$$

## Conformational entropy of a protein

Estimate the conformational entropy of myoglobin. Myoglobin has 150 residues with 6 possible conformations per residue. Assume there is a unique conformation for the folded structure.

**Solution:** The definition  $S = R \ln W$  is known as the statistical entropy. R is the gas constant and W is the number of possible conformations for a structure and  $W = M^N$ .

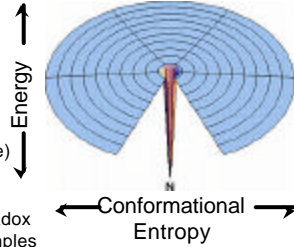
For the unfolded protein:  $W = 6^{150}$  and  $S = 150R \ln(6)$ .

For the folded protein:  $W = 1$  and  $S = 0$ .

There conformational entropy is  $\Delta_{fold}S = \Delta_{unfold}S$  and is therefore 2233 J/mol or 2.2 kJ/mol.

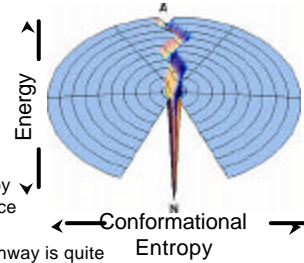
## The Levinthal Paradox

The Levinthal paradox assumes that all of the possible conformations will be sampled with equal probability until the proper one (N = native) is found. Thus, the funnel surface looks like a hole in a golf course. The paradox states that if a protein samples all  $6^M$  conformations it will take a time longer than the age of the universe to find the native fold (N) for a polypeptide where  $M = 100$  and if it takes  $10^{-11}$  seconds to sample each possible conformation!



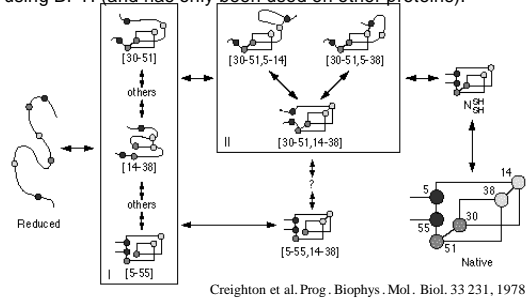
## The Pathway Model

Imagine that there is a unique pathway winds through the surface to the hole. The path starts at A and the folding goes through a unique and well-defined set of conformational changes. Here the entropy must decrease rapidly since the number of degrees of freedom in the folding pathway is quite small compared to  $6^M$ . On this diagram the configurational entropy is given by the width of the funnel and the relative by the height relative to the bottom (folded state). The vertical axis is energy NOT free energy.



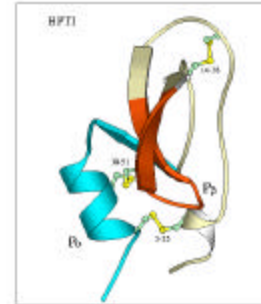
## Evidence for folding pathways

One piece of evidence for folding pathways comes from trapping disulfide intermediates. This method was pioneered by Creighton using BPTI (and has only been used on other proteins).



## Beyond pathways

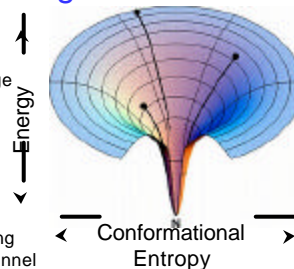
Kim et al. showed that some of the previous data and interpretations were wrong. The major 2-DS species contains the two native DS's, 30-51 and 5-55. The third disulfide is formed quite slowly because it is quite buried. It is possible to isolate a stable species with only the first two disulfides formed and the third remaining in the reduced form. Studies with a mutant in which the third DS was replaced by 2 Ala, and which folded at a similar rate to the wild type, support the idea that the trapped disulfide species have partial native-like structure. These observations and others like it can be used to the idea of a pathway into question.



Kim (1993) *Nature* 365 185

## The Folding Funnel

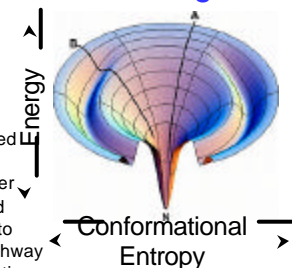
The folding funnel shown here represents the change in energy for a large number of folding paths that lead to the native configuration. There are no energy barriers. This implies that all paths have an equal probability leading to the folded state. The funnel shown here has no energy barriers and all paths lead directly to the native state. Thus, this funnel is consistent with two state folding behavior.



Dill and Chan, *Nature Struct. Biol.* (1997), 4:10-19

## Barriers and misfolding

The energy surface does not have to be a smooth trajectory. There can be barriers that will trap intermediate states. These states may then be observed to determine aspects of the folding trajectory. Whenever an intermediate is observed there will be a question as to whether this is part of a pathway or whether a funnel description is more applicable. Note that the funnel provides the possibility for misfolding. This will typically result in multiple minima in the energy landscape.



Dill and Chan, *Nature Struct. Biol.* (1997), 4:10-19