

Entropy and equilibrium

There are two aspects of interest in the link between entropy and equilibrium:

- Why systems form equilibria at all
- How the value of the equilibrium constant is related to ΔS_{total} (or ΔG).

You need to be familiar with the concept of entropy to get the most from this activity. If you are unfamiliar with entropy or how it is applied in chemistry, visit

www.entropysite.com/students_approach.html (accessed May 2007) for an introduction.

Why systems form equilibria at all

At first inspection it appears that the formation of equilibria contravenes the second law of thermodynamics – *in any spontaneous change the total entropy increases*. The total entropy change for a reaction can be calculated – $\Delta_r S_{\text{total}}$ (the *r* here indicates the molar change for the complete reaction). It is reasonable to suggest that a reaction will only proceed in the direction (forwards or backwards) for a positive $\Delta_r S_{\text{total}}$; however, for an equilibrium to form both forward and back reactions are occurring at the same time.

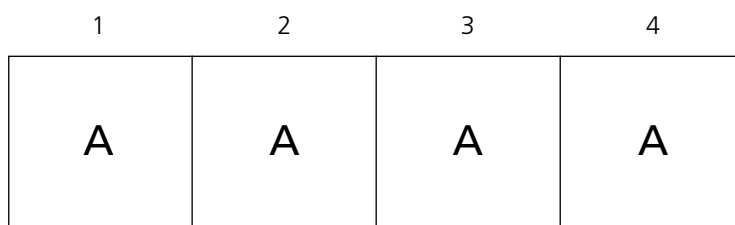
It is important to observe that $\Delta_r G$ or $\Delta_r S_{\text{total}}$ are **molar** quantities – ie the change in free energy or total entropy for 1 mole of the reactants in the balanced equation to **react completely to form products**.

We assume that to find the change in total entropy for the first tenth of a mole of reactants to form products is simply the molar quantity $\Delta_r S_{\text{total}}$ divided by 10. However, this does not take into account the fact that *mixtures tend to have greater entropy than pure substances*. We know that gases such as oxygen and nitrogen spontaneously mix, but do not spontaneously un-mix.

Developing a model of the entropy of a mixture compared to a pure substance

We are going to model the effect of the increase in entropy of a reaction when it forms an equilibrium mixture by considering the simplest kind of system $A \rightleftharpoons B$.

Let's start with a total of four particles and four positions available.



An illustration of the initial state with four particles of A

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1. Work out the number of distinct arrangements (micro-states or combinations) available to the possible mixtures formed as $A \rightleftharpoons B$. Assume that particles of A are indistinguishable from each other and particles of B are indistinguishable from each other.

Particles of A	Particles of B	Combinations (W)	$\ln W$
4	0	1	0.00
3	1	4	1.39
2	2		
1	3		
0	4		

See document *CDROM index 24E1* for a simple spreadsheet to fill in.

The final column $\ln W$ ($\log_e W$) is included because the entropy S of the system is proportional to $\ln W$ (the relationship $S = k \ln W$ was first proposed by Ludwig Boltzmann and is engraved on his tombstone).



Photo taken by Tom Schneider used with kind permission

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2. How many of each particle are there in the state with the greatest number of distinct arrangements – ie the state with highest entropy?

Enlarging the model

3. Now consider a system of 10 particles (and 10 positions) for the same reaction $A \rightleftharpoons B$. Work out the number of distinct arrangements for 0, 1, 2 and 3 particles of B, then show that your answers are consistent with the general formula:

$$\text{The number of permutations} = (A + B)! / (A! \times B!)$$

(! is the symbol for the mathematical function factorial. $5! = 5 \times 4 \times 3 \times 2 \times 1$. **Note:** $0! = 1$).

4. Use the computer spreadsheet to calculate the number of distinct arrangements (W) and $\ln W$ for a 10 particle system like that in the table below. Microsoft Excel® uses FACT(5) for $5!$

See document *CDROM index 24E2* for a simple spreadsheet to fill in.

Particles of A	Particles of B	Combinations (W)	$\ln W$
10	0	1	0.00
9	1	10	2.30
8	2	45	3.81
7	3		
6	4		
5	5		
4	6		
3	7		
2	8		
1	9		
0	10		

You should see the graph appear of $\ln W$ (proportional to the entropy) plotted against composition of the mixture.

5. Explain why the graph is steep at the edges and flattens in the middle.

Refining our model

So far our model has not taken into account the fact that the interconversion of $A \rightleftharpoons B$ will occur with a change in total entropy for the complete reaction – ie a molar $\Delta_r S_{\text{total}}$. $\Delta_r S_{\text{total}}$ is normally calculated by adding together $\Delta_r S_{\text{system}}$ and $\Delta_r S_{\text{surroundings}}$, where $\Delta_r S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$ and $\Delta_r S_{\text{surroundings}} = -\Delta_r H/T$.

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Now we are going to add to our model a component that simulates a molar total entropy change for the reaction.

6. We need two extra columns and, to keep it simple, will add one unit of entropy for every particle of B formed. Add the value in this column to $\ln W$ in the second new column to be the new S_{mixture} .

(Notice the fudge here – $\ln W$ is only proportional to the entropy change of mixing and has different units, but we are combining directly with a factor modelling $\Delta_r S_{\text{total}}$.)

See document *CDROM index 24E3* for a simple spreadsheet to fill in, and to check your answers.

Particles of A	Particles of B	Combinations (W)	$\ln W$	ΔS_{total} (molar) x B/(A+B)	S_{mixture}
10	0	1	0.00	0	0.00
9	1	10	2.30	1	3.30
8	2	45	3.81	2	5.81
7	3				
z					

7. You should see a graph of S_{mixture} against particles of B. The graph should model an equilibrium system with a small positive molar $\Delta_r S_{\text{total}}$ for the reaction. The position of equilibrium is represented by the highest point on the line – ie the state of highest entropy.
- How many particles of B will there be in the equilibrium mixture?
 - What will the value of K_c be for this equilibrium?

A larger model

8. See document *CDROM index 24E4* for a model of a 100 particle system with a slider to control the $\Delta_r S_{\text{total}}$ for the complete reaction.
- Does the reaction ever go to completion?

The model should indicate, in principle, how the equilibrium constant K varies with $\Delta_r S_{\text{total}}$.

Further thinking

9. If you have met the concept of Gibbs free energy, predict the shape of the corresponding graphs of G_{mixture} against composition when $\Delta_r G$ is positive, negative or zero.

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10. Why does ice melt at only one temperature and not form an equilibrium mixture over a range of temperatures?

There is a *Chemistry Olympiad past paper question* alternative to question 11; see *CDROM index 24AQ*.

11. Tin exists as two allotropes Sn (grey) and Sn (white). The grey allotrope of tin has a diamond like structure and the white allotrope is metallic. Under cold conditions metallic tin can develop a crumbly surface that looks like corrosion and is called *tin pest* or *tin disease*. It is often cited as a contributory factor in Napoleon's failure to conquer Russia. The winter conditions were extremely cold and supposedly the tin buttons on the soldiers' coats fell apart adding to the problems posed by the adverse weather and opposing army.
- Use the data in the table to calculate the temperature at which *white* tin changes to *grey* tin.
 - Do you expect this reaction to form an equilibrium?
 - Predict whether the interconversion is instantaneous or not.
 - Visit www.bbc.co.uk/dna/h2g2/A7241834 (accessed May 2007) for an interesting article about tin pest.

	Sn (grey)	Sn (white)
$S^\ominus / \text{J mol}^{-1} \text{K}^{-1}$	44.1	51.5
$\Delta H_{\text{atom}}^\ominus / \text{kJ mol}^{-1}$	304.2	302.1

How the value of the equilibrium constant is related to $\Delta_r G$ or $\Delta_r S_{\text{total}}$

It is beyond the scope of this activity to mathematically prove the relationship $\Delta_r G = -RT \ln K$ where $\Delta_r G = T \Delta_r S_{\text{total}}$

However, you can see how this arises graphically in a spreadsheet where ΔS_{mix} is calculated rather than modelled (*CDROM index 24E5*).

- Explore how the different stoichiometries affect the shapes of the graphs.
- Explore the effects of changing the temperature and of enthalpy and entropy changes.

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12. Use the spreadsheet calculation to answer the following questions.

- a) The equilibrium reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is quoted as having a value of K_c of 46 at 764 K. Use the spreadsheet and the data below to compare the value generated by the spreadsheet.

	$\Delta H^\theta_{\text{formation}} / \text{kJ mol}^{-1}$	$S^\theta / \text{J mol}^{-1} \text{K}^{-1}$
H₂(g)	0	131
I₂(g)	62.2	261
HI(g)	26.5	206

- b) The value of the equilibrium constant for the esterification reaction between ethanol and ethanoic acid is quoted as 4.0 at 373 K. Use the spreadsheet and the data below to estimate the standard entropy of ethyl ethanoate.

	$\Delta H^\theta_{\text{formation}} / \text{kJ mol}^{-1}$	$S^\theta / \text{J mol}^{-1} \text{K}^{-1}$
C ₂ H ₅ OH(l)	-277.1	161
CH ₃ COOH(l)	-484.5	160
CH ₃ COOC ₂ H ₅ (l)	-479.3	?
H ₂ O(l)	-285.8	70

- c) Justify the magnitude of the standard entropy of ethyl ethanoate relative to the other components of the reaction.
- d) The Haber process is quoted as having an equilibrium constant of 40.7 atm⁻² at 400 K. $\Delta H = -96 \text{ kJ mol}^{-1}$. Use the spreadsheet to find ΔS_{sys} .
- e) The value for the K_a of HNO₃(aq) is 40 mol dm⁻³.
- i) Assuming the enthalpy change for the process:
 $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ is -33 kJ mol^{-1} .
Use the spreadsheet to estimate the entropy change of the system, ΔS_{sys} .
- ii) Is the answer to part i) surprising?