Entropy and equilibrium

1. *Work out the number of distinct arrangements 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
3	1	4	1.3863
2	2	6	1.7918
1	3	4	1.3863
0	4	1	0

2. *How many of each particle are there in the state with the highest entropy?*

The mixture of 2 A and 2 B particles has the highest entropy.

Enlarging the model

3. *Now consider a system of 10 particles (and 10 positions) for the same reaction $A \rightleftharpoons B$. By working out the combinations for 0, 1, 2 and 3 particles of B, then show that your answers are consistent with the general formula:*
   The number of permutations = (A + B)!/(A! x B!).

Consider the case of 2 B particles (and 8 A particles). The first particle can be in one of 10 positions and the next in any one of nine positions. If the two particles are different there are 90 permutations, but because they are the same we need to divide by the number of times a permutation is repeated, in this case two.

For three particles of B we have 10 x 9 x 8 permutations for non-identical B particles but then each permutation is repeated 3 x 2 times. Because the B particles are identical (any one permutation of the 3 B particles could have the first B particle in one of three positions and then the second in one of 2 positions).

The pattern continues and is expressed by the formula:

The number of combinations = (A + B)!/(A! x B!)

This can be expressed mathematically as ${}^{n}C_{r}$ where n = the number of positions and r = the number of particle of B.

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4. *Use the computer spreadsheet (CDROM index 24E2) 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!*

Particles of A	Particles of B	Combinations (*W*)	ln *W*
10	0	1	0
9	1	10	2.302585093
8	2	45	3.80666249
7	3	120	4.787491743
6	4	210	5.347107531
5	5	252	5.529429088
4	6	210	5.347107531
3	7	120	4.787491743
2	8	45	3.80666249
1	9	10	2.302585093
0	10	1	0

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

The impact of introducing the first particle of B is greatest because there are no other B particles in the mixture yet that it is identical with, so the particle makes a new combination for every position available (*ie* 10). In the middle, say when we have four particles of B already, the impact is less because there are in effect only six positions left for the B particle to make combinations.

Refining our model

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* $S_{mixture}$.

Particles of A	Particles of B	Combinations (*W*)	ln *W*	ΔS total 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	120	4.79	3	7.79
6	4	210	5.35	4	9.35
5	5	252	5.53	5	10.53
4	6	210	5.35	6	11.35
3	7	120	4.79	7	11.79
2	8	45	3.81	8	11.81
1	9	10	2.30	9	11.30
0	10	1	0.00	10	10.00

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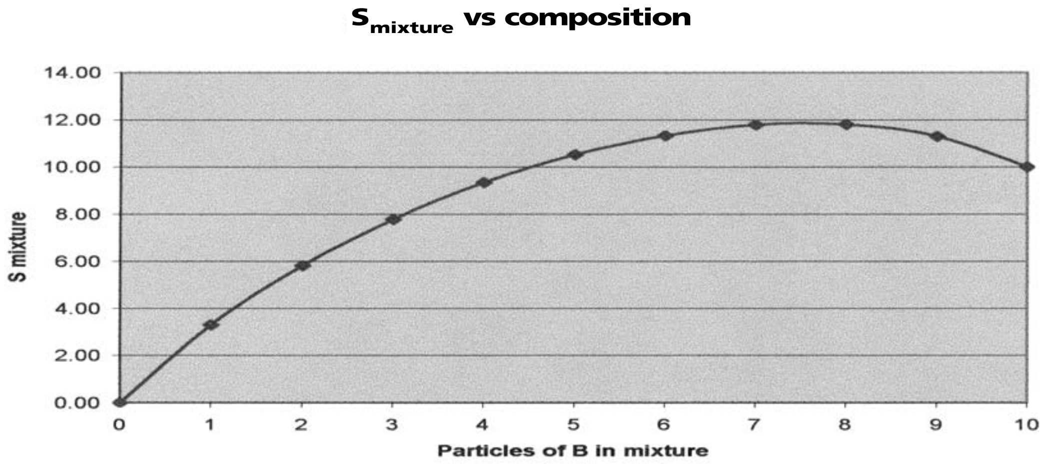

Excel® spreadsheet graph: CDROM index 24E3

7. *…The position of equilibrium is represented by the highest point on the line – ie the state of highest entropy.*
   a) How many particles of B will there be in the equilibrium mixture?

There are most likely to be seven or eight particles of B in the equilibrium mixture but we would expect some fluctuation in a dynamic system. In any one instant, for example, we might get 10 particles of B. This might seem like a large fluctuation but this is only because our model has few particles. Any real system is likely to have many more particles and therefore a stable position of equilibrium.

   b) What will the value of K_c be for this equilibrium?

K_c will be in the range of 7/3–8/2 – *ie* 2.3–4.

These values are close to one. Most K_c values are much larger or smaller than one which shows that $\Delta_r S^{\ominus}_{total}$ is frequently a more dominant factor than in the model.

A larger model

8. *…*
   a) Does the reaction ever go to completion?

No, even with a model as small as 100 particles, we do not see either complete reaction or no reaction within the range of values of $\Delta_r S^{\ominus}_{total}$ used in the model.

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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The graphs will appear as if the trend lines had undergone a reflection in the x axis. For example, see the Excel® spreadsheet *Gmix vs composition* (CDROM index 24E6) for a 100 particle model plotting G_{mixture} against composition.

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

Ice and water are in separate phases so there is *no mixing* of the two. Ice melts at the temperature at which $\Delta_r S^{\ominus}_{\text{total}} = 0$. The graph of S_{mixture} against % composition is a straight line and not a curve because the particles of ice and water cannot interchange.

11. *Tin exists as two allotropes ...*
    a) Use the data in the table to calculate the temperature at which white tin changes to grey tin.

Sn (white) → Sn (grey) $\Delta H = 302.1 - 304.2 = -2.1$ kJ mol^{-1}
$\Delta S_{\text{sys}} = 44.1 - 51.5 = -7.4$ kJ mol^{-1}
$\Delta S_{\text{Total}} = \Delta S_{\text{sys}} - \Delta H/T$
When $\Delta S_{\text{Total}} = 0$ then T $= \Delta H / \Delta S_{\text{sys}}$
$= 2100/7.4$ K
$= 284$ K

b) Do you expect this reaction to form an equilibrium?

No, because there is no entropy of mixing, the two allotropes will be pure, separate phases.

c) Predict whether the interconversion is instantaneous or not.

It seems unlikely that the reaction is instantaneous, observations suggest that the reaction is slow.

12. *Use the spreadsheet calculation to answer the following questions.*
    a) The equilibrium reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ *is quoted as having a value of* K_c *of 46 at 764 K.*

The spreadsheet gives an answer in very close agreement with this.

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.

The enthalpy change for the reaction = –3.5 kJ mol^{-1}. When this value (rounded to – 4 kJ mol^{-1}) is entered in the spreadsheet, the ΔS_{sys} required to get an equilibrium constant closest to 4 is +1 J K^{-1} mol^{-1}. The standard entropies of the other components can then be used to calculate the value for the standard entropy of ethyl ethanoate = 252 J K^{-1} mol^{-1}.

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c) Justify the magnitude of the standard entropy of ethyl ethanoate relative to the other components of the reaction.

The value calculated for the standard entropy of ethyl ethanoate is considerably larger than the entropies of the other components. There are two reasons for this. Ethyl ethanoate is a more complex molecule than any of the others, comprising more atoms joined together. Ethyl ethanoate(l) will not hydrogen bond with itself so there will be a less ordered structure in the liquid.

d) The Haber process is quoted as having an equilibrium constant of 40.7 atm^{-2} at 400 K. ΔH = -96 kJ mol^{-1}. Use the spreadsheet to find ΔS_{sys}.

$\Delta S_{\mathrm{sys}} = -209$ J K^{-1} mol^{-1}

e) The value for the K_a of $HNO_3(aq)$ is 40 mol dm^{-3}.

i) Assuming the enthalpy change for the process:
$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$ is –33 kJ mol^{-1}.
Use the spreadsheet to estimate the entropy change of the system, ΔS_{sys}.

Using the A⇌C + D sheet we get $\Delta S_{\mathrm{sys}} = -80$ J K^{-1} mol^{-1}.

ii) Is the answer to part i) surprising?

This is perhaps surprising as we might have expected a positive ΔS_{sys} – *ie* one aqueous species forming two separate aqueous species.

The ions formed strongly attract the water molecules that solvate them and cause these to form an ordered shell around the charged ions. This ordering of the solvent molecules explains the negative ΔS_{sys}.