

# Entropy and equilibrium



Chemistry for the gifted and talented  
Entropy and equilibrium

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$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At equilibrium, the concentration of  $H_2$  is 0.10 mol dm<sup>-3</sup> and the concentration of  $I_2$  is 0.10 mol dm<sup>-3</sup>. Calculate the concentration of  $HI$  at equilibrium.

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Student worksheet: CDROM index 24SW



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Discussion of answers: CDROM index 24DA



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Alternative question 11: CDROM index 24AQ



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Alternative answer 11: CDROM index 24AA



Particles of A	Particles of B	Combinations (N)	lnN
4	0	1	0.00
3	1	4	1.39
2	2		
1	3		
0	4		

Complete column C by adding the number of combinations (N) for the other mixtures of A and B.

To fill in the lnN column with the right formula simply select one of the cells in the table.

When the cursor changes into a solid cross click and drag the cross over the bottom right corner of that cell.

When the cursor changes into a solid cross click and drag the cross down to the cells in the column.

Excel will then fill the formula into the cells.

To check your answers click on the answer sheet tab below.

To return to the main activity close this document.

Excel® spreadsheets: CDROM index 24E1, 24E2, 24E3, 24E4, 24E5 and 24E6

**Topics**

Entropy and equilibrium.

**Level**

Gifted post-16 students who are motivated about understanding the fundamental concepts of entropy and equilibrium.

**Prior knowledge**

Entropy, the second law of thermodynamics (expressed in terms of  $\Delta S_{\text{total}}$ ), calculations of permutations, factorial function (!), natural logarithms, entering formulae in spreadsheets and dragging and filling-in spreadsheets.

**Other concepts**

$S = k \ln W$  and modelling.

**Rationale**

Chemistry at its best is an interconnected web of concepts, skills and facts. Very able students find the linking of concepts particularly rewarding. This activity shows the students the fundamental link between entropy and equilibrium and increases their understanding of scientific models. It highlights the importance of mathematical descriptions in physical chemistry. They also use and develop their maths and IT skills.

The activity focuses on entropy, rather than Gibbs energy, because those who have gone as far as Gibbs energy should still be able to follow a discussion based on entropy. Entropy is a more fundamental concept than Gibbs energy.

**Use**

This worksheet is designed to be used by students working individually at a computer, or during a teacher-led group discussion via a projector. Teachers may find the spreadsheets helpful (calculation 1 in particular) for use in their general teaching.

There are references in the worksheet to direct students to various Excel® spreadsheets stored on the CDROM. When they have finished working on the spreadsheets students should close the windows containing the spreadsheets – they should **not save changes** to the spreadsheets! The 100 particle model spreadsheets are set up with protection on, but more accessible sheets are available if students want to see the workings.

A more detailed alternative to question 11 is the *UK 2004 Round 1 Olympiad selection paper question 5* which is included (CDROM index 24AQ and 24AA).

**Further reading**

A more complete explanation of the connection between the entropy of mixing and equilibrium can be found in:

Keeler & Wothers, *Why chemical reactions happen*, Oxford: Oxford University Press, 2003 (distributed to secondary schools and colleges by the RSC Spring 2006).

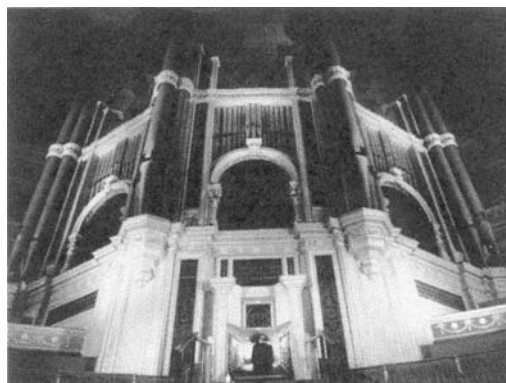
Chapter 8 should be used first.

## Entropy and equilibrium

Alternative question 11.

### Tin pest

Tin can exist as two stable allotropes:  $\beta$ -tin or white tin, which is metallic, and  $\alpha$ -tin or grey tin, which is non-metallic. The conversion from one form to the other occurs at a critical temperature,  $T_c$ . The conversion from the metallic form to the powdery non-metallic form is known as *tin pest* or *tin disease*, partly because the accompanying change in density may cause 'warts' to form on the surface.



*The organ at the Royal Albert Hall contains 150 tonnes of tin!*

Tin pest has been suggested as the cause of organ pipes disintegrating in certain cold churches (previously thought to be the work of the devil), and even as a possible reason for the failure of Captain Scott's expedition to the South Pole, when the tin solder used in the fuel cans deteriorated.

The question refers to the change: white tin  $\longrightarrow$  grey tin

You should use the following data:

	$\Delta_f H^\ominus$ /kJ mol <sup>-1</sup>	$S^\ominus$ /J K <sup>-1</sup> mol <sup>-1</sup>	Density /g cm <sup>-3</sup>	Atomic distance to nearest neighbour /pm
White tin	0	51.4	7.31	302
Grey tin	-2.09	44.1	5.75	280

11.

- a) Calculate the standard enthalpy change ( $\Delta_r H^\ominus$ ) for the change.

It is possible to calculate the standard entropy change ( $\Delta_r S^\ominus$ ) for this reaction in a similar way to the above using the standard entropy values ( $S$ ) given in the table.

- b) Calculate  $\Delta_r S^\ominus$  for this reaction.

The feasibility of any chemical process at an absolute temperature  $T$  can be determined by calculating the change in the Gibbs energy ( $\Delta_r G$ ) for the process at that temperature, where

$$\Delta_r G = \Delta_r H - T \Delta_r S .$$

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If  $\Delta_r G$  is less than zero, the process can take place. If it is greater than zero, it cannot.

- c) Calculate  $\Delta_r G$  for the change white tin  $\rightarrow$  grey tin at room temperature, 25 °C.
- d) Which allotrope of tin is stable at room temperature? Justify your answer.
- e) Calculate the temperature,  $T_c$ , at which both allotropes are in equilibrium.
- f) Calculate the percentage increase in volume as white tin converts to grey tin.
- g) Which allotrope possesses the greater coordination number? Justify your answer.



## Entropy and equilibrium

Alternative question 11.

### Tin pest

#### Answers

a)  $\Delta_r H^\ominus = -2.09 \text{ kJ mol}^{-1}$

b)  $\Delta_r S^\ominus = 44.1 - 51.4$   
 $= -7.30 \text{ J K}^{-1} \text{ mol}^{-1}$

c)  $25 \text{ }^\circ\text{C} = 298 \text{ K}$   
 $\Delta_r G = \Delta_r H - T \Delta_r S$   
 $= -2090 - (298 \times -7.3)$   
 $= 85.4 \text{ J mol}^{-1}$

d) White, because  $\Delta_r G > 0$  at room temperature.

e)  $T = (\Delta_r H - \Delta_r G) / \Delta_r S$   
 $= (-2090 - 0) / -7.3$   
 $= 286 \text{ K (13 }^\circ\text{C)}$

f) Volume of 1 g white tin =  $1 / 7.31 = 0.137 \text{ cm}^3$   
Volume of 1 g grey tin =  $1 / 5.75 = 0.174 \text{ cm}^3$   
Percentage volume increase  
 $= [(0.174 - 0.137) / 0.137] \times 100 = 27.0 \%$

g) White tin has a greater coordination number because it is denser so the atoms are more tightly packed. There is a larger distance to its nearer neighbours which implies it has more neighbours (especially since it is more dense).

This question was taken from the *UK Olympiad selection competition 2004*, Round 1, question 5.

## 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  $\Delta S_{\text{total}}$  (or  $\Delta G$ ).

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](http://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.

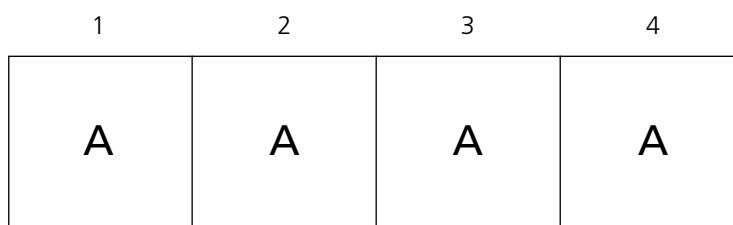
It is important to observe that  $\Delta_r G$  or  $\Delta_r S_{\text{total}}$  are **molar** quantities – ie the change in free energy or total entropy for 1 mole of the reactants in the balanced equation to **react completely to form products**.

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**

*Continued on page 2*



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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*

*continued on page 3*



# Chemistry for the gifted and talented

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  $\Delta_r S_{\text{surroundings}} = -\Delta_r H/T$ .

*continued on page 4*





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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  $S_{\text{mixture}}$ .

(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)	$\ln W$	$\Delta S_{\text{total}}$ (molar) x B/(A+B)	$S_{\text{mixture}}$
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  $S_{\text{mixture}}$  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  $G_{\text{mixture}}$  against composition when  $\Delta_r G$  is positive, negative or zero.

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# Chemistry for the gifted and talented

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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](http://www.bbc.co.uk/dna/h2g2/A7241834) (accessed May 2007) for an interesting article about tin pest.

	Sn (grey)	Sn (white)
$S^\theta / \text{J mol}^{-1} \text{K}^{-1}$	44.1	51.5
$\Delta H^\theta_{\text{atom}} / \text{kJ mol}^{-1}$	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  $\Delta S_{\text{mix}}$  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.

	$\Delta H^\theta_{\text{formation}} / \text{kJ mol}^{-1}$	$S^\theta / \text{J mol}^{-1} \text{K}^{-1}$
<b>H<sub>2</sub>(g)</b>	0	131
<b>I<sub>2</sub>(g)</b>	62.2	261
<b>HI(g)</b>	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 <sub>2</sub> H <sub>5</sub> OH(l)	-277.1	161
CH <sub>3</sub> COOH(l)	-484.5	160
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> (l)	-479.3	?
H <sub>2</sub> 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<sup>-2</sup> at 400 K.  $\Delta H = -96 \text{ kJ mol}^{-1}$ . Use the spreadsheet to find  $\Delta S_{\text{sys}}$ .
- e) The value for the  $K_a$  of HNO<sub>3</sub>(aq) is 40 mol dm<sup>-3</sup>.
- i) Assuming the enthalpy change for the process:  
 $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$  is  $-33 \text{ kJ mol}^{-1}$ .  
Use the spreadsheet to estimate the entropy change of the system,  $\Delta S_{\text{sys}}$ .
- ii) Is the answer to part i) surprising?

## 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 =  $(A + B)! / (A! \times B!)$ .

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  $10 \times 9 \times 8$  permutations for non-identical B particles but then each permutation is repeated  $3 \times 2$  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 =  $(A + B)! / (A! \times B!)$

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

*continued on page 2*



# Chemistry for the gifted and talented

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.

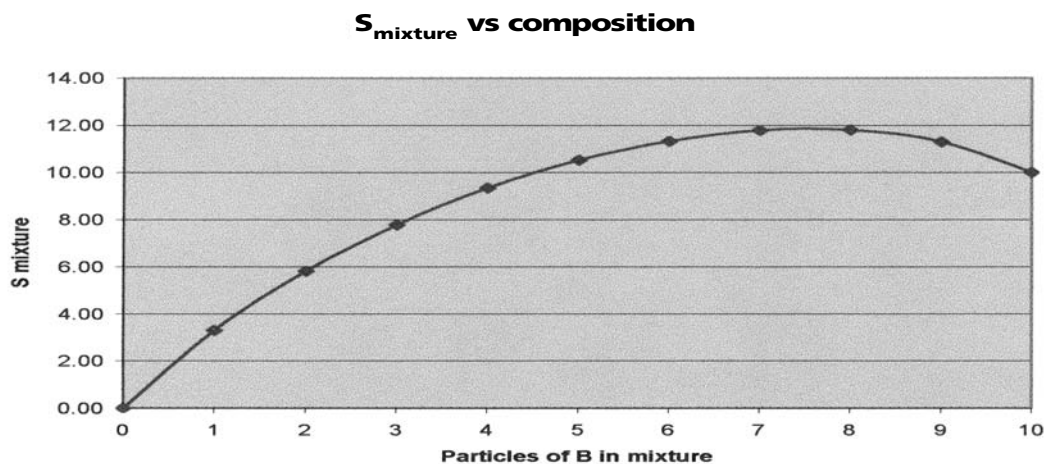
The impact of introducing the first particle of B is greatest because there are no other B particles in the mixture yet that it is identical with, so the particle makes a new combination for every position available (ie 10). In the middle, say when we have four particles of B already, the impact is less 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  $S_{\text{mixture}}$ .

Particles of A	Particles of B	Combinations ( $W$ )	$\ln W$	$\Delta S$ total x B/(A+B)	$S_{\text{mixture}}$
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

continued on page 3



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  $\Delta_r S_{\text{total}}^\ominus$  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  $\Delta_r S_{\text{total}}^\ominus$  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  $G_{\text{mixture}}$  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 *G<sub>mix</sub> vs composition* (CDROM index 24E6) for a 100 particle model plotting  $G_{\text{mixture}}$  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  $\Delta_r S_{\text{total}}^{\ominus} = 0$ . The graph of  $S_{\text{mixture}}$  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.

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

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  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  is quoted as having a value of  $K_c$  of 46 at 764 K.

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

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

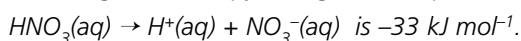
The value calculated for the standard entropy of ethyl ethanoate is considerably larger than the entropies of the other components. There are two reasons for this. Ethyl ethanoate is a more complex molecule than any of the others, comprising more atoms joined together. Ethyl ethanoate(l) will not hydrogen 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  $40.7 \text{ atm}^{-2}$  at 400 K.  $\Delta H = -96 \text{ kJ mol}^{-1}$ . Use the spreadsheet to find  $\Delta S_{\text{sys}}$ .

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

e) The value for the  $K_a$  of  $\text{HNO}_3(\text{aq})$  is  $40 \text{ mol dm}^{-3}$ .

i) Assuming the enthalpy change for the process:



Use the spreadsheet to estimate the entropy change of the system,  $\Delta S_{\text{sys}}$ .

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

ii) Is the answer to part i) surprising?

This is perhaps surprising as we might have expected a positive  $\Delta S_{\text{sys}}$  – i.e. 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  $\Delta S_{\text{sys}}$ .