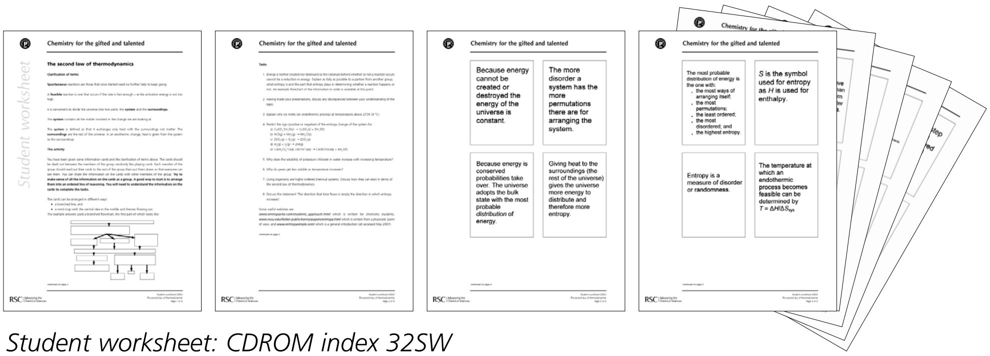
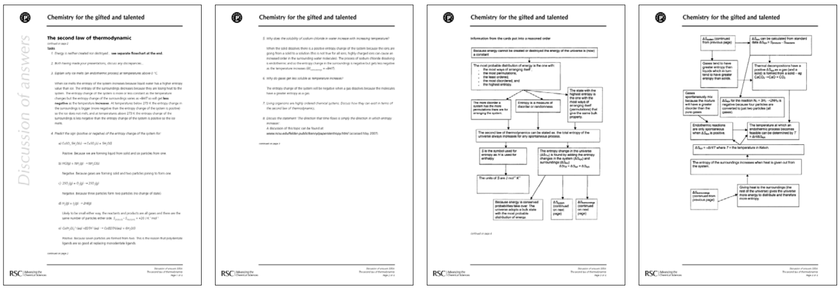
# The second law of thermodynamics



*Student worksheet: CDROM index 32SW*



*Discussion of answers: CDROM index 32DA*

**Topics**

System, surroundings, disorder, spontaneous changes, entropy and the second law of thermodynamics.

**Level**

More able post-16 students.

**Prior knowledge**

Enthalpy changes and $\Delta H$.

**Rationale**

Entropy is a topic that very able post–16 chemistry students should meet irrespective of whether it forms part of their course specification or not. Gifted students are often attracted by the fundamental ideas and the second law of thermodynamics is both fundamental and surprising the first time you meet it. This activity aims to introduce the topic in a way that uses the students' synthesis skills to piece together several pieces of information. Answers are available and the students explain their understanding to one another thus reinforcing their ideas.

**Use**

This is a group activity best used with groups of three to five students, but could be done by two or even a single student – with some adaptation. If entropy is part of the course then this activity can be used as an introduction to the topic with the whole group or a summary exercise at the end. If used as an introduction with a mixed ability group, trialling suggests that they may not assimilate all the information, but that it will stimulate questions and interest.

A website that might be used to introduce some of the terms is *www.mhhe.com/physsci/chemistry/chang7/esp/folder_structure/en/m4/s1/index.htm* (accessed May 2007). If used as extension work for the most able students, it may not need much input from a teacher. It may also stimulate sufficient interest for them to read up on the topic.

The students should be split up into groups of three to five. They should each be given the worksheet and one set of information cards per group. If you plan to reuse the cards they are best produced in a different colour for each set. Once they have arranged the cards into a reasoned order they should be given the example arrangement of information to aid their explanation to another student. They can then tackle the remainder of the questions.

The *Discussion of answers* sheet should be given so they can review their own or each others' ideas.

This symbol means those questions are best tackled as a discussion if a group of students is doing this activity. Written answers are not expected. Some of the questions asked towards the end of the activity are quite involved and may be best tackled in a separate lesson once the main ideas have sunk in.

Student worksheet

# The second law of thermodynamics

### Clarification of terms

**Spontaneous** reactions are those that, once started, need no further help to keep going.

A **feasible** reaction is one that occurs if the rate is fast enough – *ie* the activation energy is not too high.

It is convenient to divide the universe into two parts: the **system** and the **surroundings.**

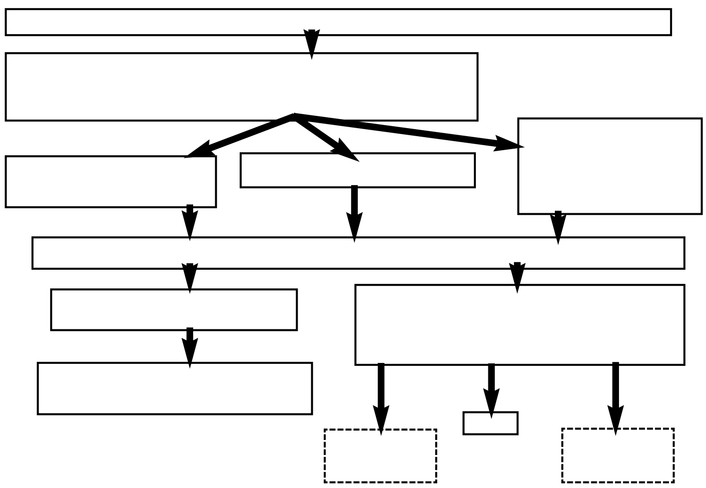
The **system** contains all the matter involved in the change we are looking at.
The **system** is defined so that it exchanges only heat with the surroundings, not matter.
The **surroundings** are the rest of the universe.
In an exothermic change, heat is given from the system to the surroundings.

### The activity

You have been given some information cards and the clarification of terms above. The cards should be dealt out between the members of the group randomly like playing cards. Each member of the group should read out their cards to the rest of the group then put them down so that everyone can see them. You can share the information on the cards with other members of the group. **Try to make sense of all the information on the cards as a group. A good way to start is to arrange them into an ordered line of reasoning. You will need to understand the information on the cards to complete the tasks.**

The cards can be arranged in different ways:
- a branched line; and
- a mind map with the central idea in the middle and themes flowing out.

The example answers used a branched flowchart, the first part of which looks like:



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**Tasks**

1. Energy is neither created nor destroyed, so the rationale behind whether or not a reaction occurs cannot be a reduction in *energy*. Explain as fully as possible to a partner from another group what entropy is and the part that entropy plays in determining whether a reaction happens or not. An example flowchart of the information in order is available at this point.

2. Having made your presentations, discuss any discrepancies between your understanding of the topic.

3. Explain why ice melts (an endothermic process) at temperatures above 273K (0 °C).

4. Predict the sign (positive or negative) of the entropy change of the system for:
   a) $CuSO_4.5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(l)$
   b) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
   c) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
   d) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
   e) $Co(H_2O)_6^{2+}(aq) + EDTA^{2-}(aq) \rightarrow Co(EDTA)(aq) + 6H_2O(l)$.

5. Why does the solubility of potassium chlorate in water increase with increasing temperature?

6. Why do gases get less soluble as temperature increases?

7. Living organisms are highly ordered chemical systems. Discuss how they can exist in terms of the second law of thermodynamics.

8. Discuss the statement 'The direction that time flows is simply the direction in which entropy increases'.

Some useful websites are:
***www.entropysite.com/students_approach.html*** which is written for chemistry students; ***www.ncsu.edu/felder-public/kenny/papers/entropy.html*** which is written from a physicist's point of view; and ***www.entropysimple.com/*** which is a general introduction (all accessed May 2007).

*continued on page 3*

Because energy cannot be created or destroyed the energy of the universe is constant.

The more disorder a system has, the more permutations there are for arranging the system.

Because energy is conserved, probabilities take over. The universe adopts the bulk state with the most probable *distribution* of energy.

Giving heat to the surroundings (the rest of the universe) gives the universe more energy to distribute and therefore more entropy.

*continued on page 4*

The most probable distribution of energy is the one with:

- the most ways of arranging itself;
- the most permutations;
- the least ordered;
- the most disordered; and
- the highest entropy.

*S* is the symbol used for entropy, as *H* is used for enthalpy.

Entropy is a measure of disorder or randomness.

The temperature at which an endothermic process becomes feasible can be determined by $T = \Delta H/\Delta S_{sys}$

*continued on page 5*

$\Delta S_{sys}$ for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ is negative because four particles are converted to just two particles (all gases).

Gases tend to have greater entropy than liquids, which in turn tend to have greater entropy than solids.

The second law of thermodynamics can be stated as: the total entropy of the universe always increases for any spontaneous process.

The entropy change in the universe ($\Delta S_{Tot}$) is found by adding the entropy changes in the system ($\Delta S_{sys}$) and surroundings ($\Delta S_{sys}$)
$\Delta S_{Tot} = \Delta S_{sur} + \Delta S_{sys}$

*continued on page 6*

The entropy of the surroundings increases when heat is given out from the system.

$\Delta S_{sur} = -\Delta H/T$ where $T$ = the temperature in degrees Kelvin.

The units of S are J $mol^{-1}$ $K^{-1}$.

Endothermic reactions are only spontaneous when $\Delta S_{sys}$ is positive.

continued on page 7

Gases spontaneously mix because the mixture will have a greater disorder than the pure gases.

$\Delta S_{sys}$ can be calculated from standard data

$\Delta S_{sys} = S_{products} - S_{reactants}$

The state with the highest entropy is the one with the most ways of arranging itself (permutations) that give the same bulk property.

Thermal decompositions have a positive $\Delta S_{sys}$ because a gas (and a solid) is formed from a solid – *eg*

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Discussion of answers

## The second law of thermodynamics

**Tasks**

1. *Energy is neither created nor destroyed...* **see separate flowchart at the end.**

2. *Both having made your presentations, discuss any discrepancies...*

3. *Explain why ice melts (an endothermic process) at temperatures above 0 °C.*

   When ice melts the entropy of the system increases because liquid water has a higher entropy value than ice. The entropy of the surroundings decreases because they are losing heat to the system. The entropy change of the system is more or less constant as the temperature changes, but the entropy change of the surroundings varies as $-\Delta H/T$ so will get **less negative** as the temperature **increases**. At temperatures below 273 K the entropy change in the surroundings is bigger (more negative than the entropy change of the system is positive), so the ice does not melt. At temperatures above 273 K the entropy change of the surroundings is less negative than the entropy change of the system is positive, so the ice melts.

4. *Predict the sign (positive or negative) of the entropy change of the system for:*

   a) $CuSO_4.5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(l)$

   Positive. Because we are forming liquid from solid and six particles from one.

   b) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

   Negative. Because gases are forming solid and two particles are joining to form one.

   c) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

   Negative. Because three particles form two particles (no change of state).

   d) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

   Likely to be small either way. The reactants and products are all gases and there are the same number of particles either side. $S_{products} - S_{reactants} = +20$ J K$^{-1}$ mol$^{-1}$.

   e) $Co(H_2O)_6^{2+}(aq) + EDTA^{2-}(aq) \rightarrow Co(EDTA)(aq) + 6H_2O(l)$

   Positive. Because seven particles are formed from two. This is the reason that polydentate ligands are so good at replacing monodentate ligands.

*continued on page 2*

5. *Why does the solubility of potassium chlorate in water increase with increasing temperature?*

   When the solid dissolves there is a positive entropy change of the system because the ions are going from a solid to a solution (**Note:** this is not true for all ions, highly charged ions can cause an increased order in the surrounding water molecules).

   The process of sodium chloride dissolving is endothermic and so the entropy change in the surroundings is negative but gets less negative as the temperature increases ($\Delta S_{surroundings} = -\Delta H/T$).

6. *Why do gases get less soluble as temperature increases?*

   The entropy change of the system will be negative when a gas dissolves because the molecules have a greater entropy as a gas.

7. *Living organisms are highly ordered chemical systems. Discuss how they can exist in terms of the second law of thermodynamics.*

8. *Discuss the statement 'The direction that time flows is simply the direction in which entropy increases'.*
   A discussion of this topic can be found at:
   *www.ncsu.edu/felder-public/kenny/papers/entropy.html* (accessed May 2007).

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**Information from the cards put into a reasoned order**

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Because energy is conserved, probabilities take over. The universe adopts a bulk state with the most probable *distribution* of energy.

$\Delta S_{system}$ (continued on next page)

$\Delta S_{surroundings}$ (continued on next page)

*continued on page 4*

$\Delta S_{system}$ (continued from previous page)

$\Delta S_{sys}$ can be calculated from standard data $\Delta S_{sys} = S_{products} - S_{reactants}$

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$\Delta S_{surroundings}$ (continued from previous page)

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