Pheromones

Introduction
Teachers who have not used the problems before should read the section Using the problems before starting.

Prior knowledge
Knowledge that ethers are chemically unreactive, concept of bond length and familiarity with Avogadro's number. A detailed knowledge is unnecessary as students are encouraged to consult textbooks and data books during the exercise.

Resources
Scientific calculators, data books and textbooks should be available for reference.

Group size
3–4.

Possible solutions
Question **(ii)** can be answered precisely; all the others require – to a greater or lesser extent – judgement and/or reasonable 'guesstimates'.

(i) Properties of saturated hydrocarbons; if students have met ethers they may over-estimate the flammability of the pheromone[1] by comparing it with the volatile ethoxyethane. They are not expected to know about the epoxide ring, but in the trials some groups did expect that the ring would be unstable.[2] The physical properties will be similar to those of a C_{19} alkane, one of the bigger molecules in diesel, so it probably would (just) be detectable by smell if left open in a small room.

The following calculations offer an excellent opportunity for discussing significant figures.

(ii) Formula $C_{19}H_{38}O$; molecular mass = 282
1 mole or 6.02×10^{23} molecules has a mass of 282 g

$$\text{the number of molecules in } 10^{-13}\text{ g} = \frac{6.02 \times 10^{23} \times 10^{-13}}{282} = 2 \times 10^{8}$$

(iii) Distance between carbons (C–C single bond length) = 0.154 nm
(The actual distance will be 80 % of this because sin 54° = 0.8; in terms of order of magnitude this can be ignored.)

The approximate length of the molecule is therefore 17 x 0.15 nm = 2.5 nm (2.5×10^{-9} m).

Thus the molecules in 10-13 g of pheromone placed end to end will stretch approximately $2 \times 10^{8} \times 2.5 \times 10^{-9}$ m or about 0.5 m.

(iv) The data given in the passage are inadequate for such a calculation, but it is sometimes necessary to make decisions based on inadequate information. Students are asked about the maximum volume where there is a possibility of the pheromone being sensed by the moth. If they are stuck, it helps to ask, 'What information do you need to know in order to do the calculation?', and then tell them to make guesses at these figures. The students' assumptions could well be quite different from those made below, but could be equally valid.

Some possible assumptions are that:

- the male gypsy moth can detect a single molecule of pheromone;
- the molecule has to be present in the approximate volume of a gypsy moth; and
- the volume of a male gypsy moth is about 0.5 cm3 or 0.5 x 10-3 dm3.

On this basis, 1 molecule per 0.5×10^{-3} dm^3 is required.

There are 2×10^8 molecules, so the volume is $0.5 \times 10^{-3} \times 2 \times 10^8 = 105$ dm^3 or 100 m^3, ie a large room 10 m x 4 m x 2.5 m high.

This will be a maximum figure: the real figure is likely to be substantially smaller.

Suggested approach

During trialling the following instructions were given to students and proved to be extremely effective:

1. Discuss each of the problems in turn. In each case decide whether a precise answer is appropriate; where it isn't, use your common sense to make sensible estimates. You can divide the work amongst yourselves but keep each other informed of progress.
Discussion can play a vital part in working out solutions to problems like this where divergent thinking is needed. Several minds working together on a problem can stimulate ideas that one on its own could not manage. About 10 minutes should be spent on the initial discussion, with further discussion as required.

2. Describe briefly what you did. Include how and why you decided upon the estimates.

3. Working as a group, prepare a short (ca 5-minute maximum) presentation to give to the rest of the class. If possible all group members should take part: any method of presentation (such as a blackboard, overhead projector, etc) can be used.
Outline the problem, describe what you did and explain the approximations and 'guesstimates' you made. After the presentation, be prepared to accept and answer questions and to discuss what you did with the rest of the class.

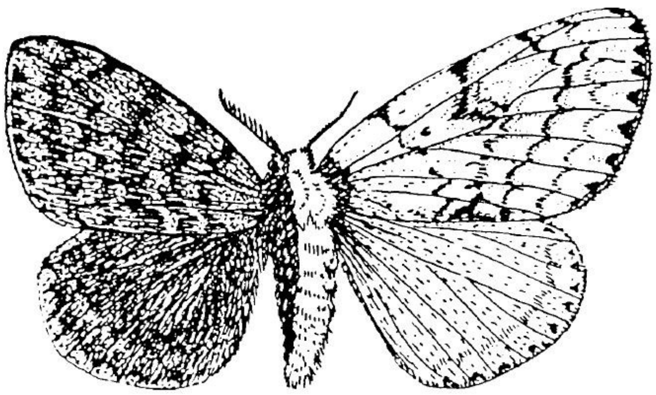
Notes

If you decide to use any of the following information it could be supplied after the presentation, or as a handout.

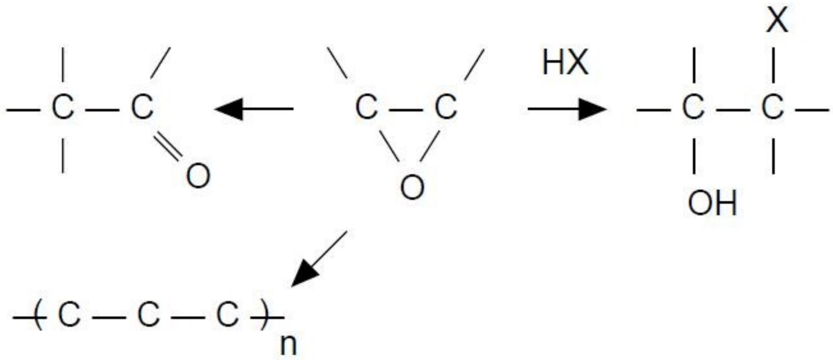
1. The gypsy moth is Lymantria dispa.

The male is smaller than the female and has feather-like receptors for the pheromone on its two antennae. The pheromone is detected as it passes through these and it is possible that the receptors can detect single molecules of the pheromone. In the open air, the pheromones tend to come as a pulsed flow of plumes or vortices which can give rise to relatively high concentrations at quite large distances from the female.
The picture of the gypsy moth on the worksheet looks peculiar because it is! Its left side is male and its right side is female because of loss of a chromosome at the first cell division.
Another moth is the winter moth Operophtera brumata – the female of this species is flightless, and emits pheromones to advertise herself to males.

Pheromones are also used as alarm signals by, for example, ants. The majority are in the C_6 to C_{10} range with a lower molecular mass than attractant pheromones; their volatility allows rapid dispersal and rapid response by other ants. For example, the alarm pheromone of the ant Lasius alienus is mainly undecane and these ants are responsive to concentrations of 10^7 to 10^8 molecules per cubic centimetre.



2. Most ethers are unreactive apart from their flammability, however the epoxide ring is so strained (bond angles 60° rather than the tetrahedral 108°) that this ether readily undergoes rearrangement to a ketone, ring opening with nucleophilic reagents (HX), or polymerisation. The product of each of these reactions is less strained than the epoxide.



The reagent HX can be water or an alcohol or an amine. One example of this is the epoxy adhesive Araldite™. Reaction of one component (which contains epoxide rings) with the other (which contains amino groups) leads to the formation of new covalent bonds and the cross-linking and setting of the resin.
Reaction of the hydroxyl groups on wood, glass or china bonds the Araldite™ to these surfaces.
Cigarette smoke contains the hydrocarbon benzpyrene which is oxidised to an epoxide in our bodies. This in return reacts with amino groups in our DNA, hence the genetic message cannot be replicated accurately and this may lead to cancer tumours in the throat or lungs.

Pheromones

(i) Suggest some chemical and physical properties of the pheromone described below. Do you think you would be able to smell it if a little was placed on a saucer in a small room with you?

(ii) How many molecules are there in the mass (10^{-13} g) of the sex attractant given in the text?

(iii) Estimate how far this number of molecules would stretch if they were straightened out and placed end to end.

(iv) The male moth senses the pheromone using feather-like receptors on its two antennae. The pheromone molecules have to move into air for the moth to respond. You may assume that the molecules diffuse evenly through air.

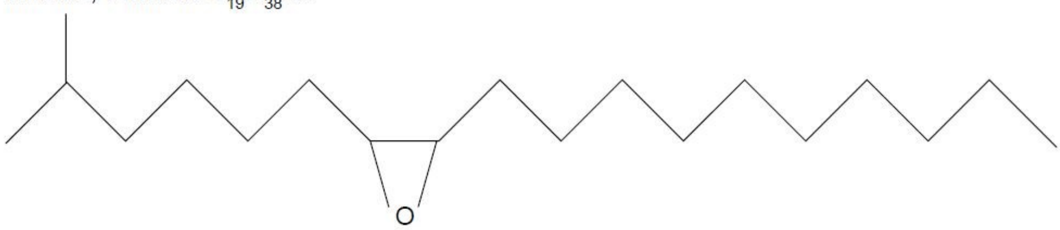
Estimate the maximum volume of air that 10^{-13} g of the pheromone can be dispersed into with any possibility of being sensed by a male gypsy moth. This problem is not unusual. Many real-life problems do not have simple definitive solutions. Sometimes a precise answer just does not exist, but more often the solution depends upon the assessment of imprecise ('soft') data, the balance of probabilities, and/or the attitudes of the person concerned.

We know that sometimes we make decisions that with hindsight will be incorrect; the decisions we make depend on how important we perceive each factor to be at that time and we know that sometimes we will get it wrong, ie you will have to make sensible guesstimates from 'soft' data in **(iv)**.

One of the most fascinating approaches to insect control involves pheromones. These are chemicals excreted externally and may serve ... to attract a mate .... Sex attractants are usually excreted by the female to attract males. These compounds are detectable in extremely low concentration by males, and can be used to lure males into traps or to disorient them. Field tests show that the sex attractant of the gypsy moth is effective at amounts of 10^{-13} g in the field. It is interesting that the first claim, in 1961, for having discovered the structure of the attractant was wrong. Research in this area is difficult. In 1967 researchers used the abdominal tips – which contain the glands that produce the sex attractant – of hundreds of thousands of female gypsy moths to isolate a minute amount of the attractant, and it was synthesised three years later.

B. Selinger, *Chemistry in the marketplace*, 4th ed, 173, 1992.

The sex attractant was a straight-chain alkane, with a branching methyl group at one end and a three-membered ether (or more properly epoxide) ring near the middle, formula $C_{19}H_{38}O$.



You should refer to any sources of information that you think might help such as your notebooks, textbooks and data books. Ask for assistance if you get stuck.