# Liquid and solid water; the growth of ice crystals

## **Time**

1-2 h (depending on approach).

### **Curriculum links**

Structure and bonding, hydrogen bonds.

# **Group size**

1-4 (depending on approach).

# Materials and equipment

#### Materials per group

- ice
- water.

#### **Equipment per group**

- molecular models
- laboratory glassware eg beakers
- measuring cylinders
- thermometer
- stop-watch
- safety glasses.

# Safety

Eye protection must be worn if any hazardous practical work is undertaken. Observing ice melting is not hazardous though work with supercooled water could be.

#### Risk assessment

It is the responsibility of the teacher to carry out a suitable risk assessment if practical work is undertaken.

This is an open-ended problem solving activity, so the guidance given here is necessarily incomplete. Teachers need to be particularly vigilant, and a higher degree of supervision is needed than in activities which have more closed outcomes. Students must be encouraged to take a responsible attitude towards safety, both their own and that of others. In planning an activity students should always include safety as a factor to be considered. Plans should be checked by the teacher before implementing them.

You must always comply with your employer's procedures and in some cases may decide that a particular activity is inappropriate in your situation. Further information on Health and Safety should be obtained from reputable sources such as CLEAPSS [http://science.cleapss.org.uk/] in England, Wales and Northern Ireland and, in Scotland, SSERC [https://www.sserc.org.uk/].

# Commentary

Liquid water is made up of clusters of water molecules joined together by hydrogen bonds which are continually breaking and reforming. As they turn into solid ice they become fixed into the three

dimensional pattern of the crystal. The hydrogen bonds hold the molecules further apart in ice so that it is less dense than water.

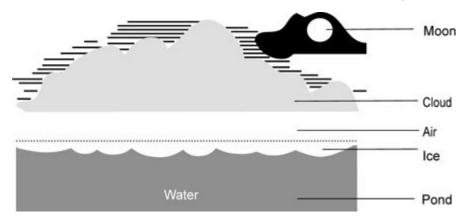
This activity is intended to encourage students to think more deeply about the process of freezing. After learning about hydrogen bonding the students may explore the arrangement of the atoms in space by building a model of an ice structure. They can work in groups to do this, each student constructing a few molecules and then joining them together. Orbital molecular models are very suitable. This in itself is an exercise in group problem solving and may be done as a competition.

#### Possible answers

(i) The students should be able to arrive at an approximate value from their own experience. This should be about  $3 \times 10^{-3}$  mm s<sup>-1</sup>. It is also possible to arrive at an answer by calculation:

#### Mathematical treatment of the freezing of a pond

There are two main methods of calculation, both based on the simple model:



Let the air temperature above the ice remain steady at  $\theta$ °C. The temperature at the interface between the ice and the water is assumed to be 0°C. The latent heat (L) is conducted away upwards.

(1) This method uses latent heat and thermal conductivity to calculate the heat losses.

density of ice p kg m<sup>-3</sup> is given by

$$\rho = \frac{m}{V}$$

where m is mass in g, V is volume in m<sup>3</sup>

$$\rho\!=\!\frac{m}{Ax}$$
 where A is area in m², and x is thickness in metres

$$m = Apx$$

Quantity of heat released when a given mass m of liquid condenses is given by mL, where L is the latent heat of fusion at 0°C

So quantity of heat released = mL = ApxL

hence if the ice thickens at a rate of 
$$\frac{dx}{dt}$$
 then loss of heat =  $\frac{dx}{dt}$ 

However, rate of loss of heat is also given by k multplied by the temperature gradient, where k is the thermal conductivity in  $J s^{-1} m^{-1} K^{-1}$ 

Let the temperature be  $\theta$ , so that

rate of loss of heat = 
$$\frac{k(\theta - 0)}{x} = \frac{k\theta}{x}$$

Therefore 
$$A\rho L \frac{dx}{dt} = \frac{k\theta}{x}$$

$$\frac{dx}{dt} = \frac{k\theta}{xA\rho L}$$

Let A be unit area, 1 m<sup>2</sup>,

rate of increase in thickness of ice =  $\frac{k\theta}{x\rho l}$ 

Data  $k = 2.1 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ 

 $L = 333 \text{ kJ kg}^{-1s}$ 

 $\rho = 0.92 \times 10^3 \text{ kg m}^{-3}$ 

 $x = 1.0 \times 10^{-2} \text{ m}$ 

If it is assumed that the air temperature above the ice is -5°C, then the rate of freezing is given by

$$\frac{2.1\times5}{333\times10^{^{3}}\times0.92\times10^{^{3}}\times1.0\times10^{^{-2}}}\,m~s^{^{-1}}$$

The ice is therefore increasing in thickness at a rate of  $3 \times 10^{-3}$  mm s<sup>-1</sup>.

(2) This more rigorous method reaches the same final equation.

The rate at which the ice thickens is limited by the thermal conductivity (k) of the ice which has already formed.

Let ρ kg m<sup>-3</sup> be the density of the ice at 0°C and k Js<sup>-1</sup> m<sup>-1</sup> K<sup>-1</sup> its thermal conductivity.

At any instant t seconds from the start of freezing, let the thickness of the ice be x metres and let the thickness increase by a small amount  $\delta x$  in a small further instant of time  $\delta t$ .

Consider unit area of the surface.

Rate of flow of heat = k multiplied by the temperature gradient

In time  $\delta t$  the volume of ice formed will be x m³ (since we are considering unit area of surface). The mass of ice formed will therefore be  $\rho\delta x$  kg and the quantity of heat flowing through the ice will be  $L\rho\delta x$  joules, where L is latent heat of fusion at 0°C (J kg<sup>-1</sup>). So, the rate of flow of heat through the ice is given by  $\frac{L\rho\delta x}{\delta t}$  Js<sup>-1</sup>.

The lower surface of the ice is at 0°C and the upper at  $-\theta$ °C,

so the temperature gradient is.  $\frac{\theta}{x}$ 

It follows from the relationship above that

$$\frac{\mathsf{L}\rho\delta x}{\delta t} = \frac{\mathsf{k}\theta}{x}$$

In the limit, 
$$\frac{dx}{dt} = \frac{k\theta}{L\rho x}$$

The rate of thickening of the ice,  $\frac{dx}{dt}$ , is therefore directly

proportional to  $\theta$  and indirectly proportional to the existing thickness x.

Rate of increase of thickness of ice =  $\frac{k\theta}{L\rho x}$ 

where  $\rho$  is the density of ice, t is the time from the start of freezing and x is the thickness.

Using the same data as before, the rate of freezing is given by

$$\frac{2.1\times5}{333\times10^3\ 0.92\times10^3\times1.0\times10^{-2}}\,ms^{-1}$$

The ice is therefore increasing in thickness at a rate of  $3 \times 10^{-3}$  mm s<sup>-1</sup>.

(ii) Students could design an experiment to investigate the rate of freezing (or melting). A very simple approach would be to immerse a large block of ice in water and to observe the rate at which it melts. Alternatively, ice could be placed in a funnel.

A more accurate method, which is described in the literature, is to observe the formation of ice crystals in thin (ca 1 mm internal diameter) polythene tubes. The tubes are filled with water and placed in a bath at a temperature below 0°C. Freezing of the supercooled water in the tube is initiated at one end and the growth velocity of the ice along the tube is measured with a stop watch. Under these conditions the latent heat can be dissipated into the surrounding liquid. This takes place more rapidly than conductive transfer through solid ice.

(iii) At 0°C, density of ice = 
$$0.92 \times 10^3 \text{ kg m}^{-3}$$

density of water =  $1.00 \times 10^3 \text{ kg m}^{-3}$ 

The structure of ice is open. Building a three dimensional model is a very effective way of seeing that a decrease in density is likely to occur when water freezes.

(iv) The answer to (i) applies to the formation of ice on the surface of a pond. Ice crystals can grow in supercooled liquid water or by sublimation from the vapour phase. The rates may be more than one million times greater than the value above.

The mechanisms that control the rate of growth are:

- (a) transport of the molecules to the point of growth;
- (b) binding of the molecules into the crystal; and
- (c) removal of the latent heat from the interface.

In the case of a layer of ice on a pond the last process is very slow and is the rate-determining step. The rate at which the latent heat is conducted away slows down as the ice thickens. It can be shown that it is inversely proportional to the thickness (see (i)). When the ice has reached a certain thickness the rate will become effectively zero so that the pond will never freeze solid.

## **Extension**

This topic lends itself well to a discussion based on 'What if?' Students could discuss what would happen if ice were not less dense than water, if it was a good conductor of heat *etc*.

When ice grows in a living system the process causes violent changes within the cells. Cryobiologists look at the biological effects of this phase change. They study the effects of low temperature on living things – food preservation is an important application.<sup>3</sup>

The phase change that occurs when a liquid metal solidifies is of great importance in metallurgy.<sup>4</sup> Again heat dissipation is significant as it can determine the direction of growth of crystals in the melt. By controlling the heat flow it is possible to produce a turbine blade made of a single crystal.

## References

- 1. N. H. Fletcher, The chemical physics of ice. Cambridge: CUP, 1970.
- 2. SATIS 16-19: Science and technology in society, A. Hunt (ed). Hatfield: ASE, 1990.
- **3.** *Nuffield advanced science chemistry food science, A special study,* (revised edn). London: Longman, 1984.
- **4.** Nuffield advanced science chemistry metals as materials, A special study, (revised edn). London: Longman, 1984.

# Acknowledgement

This activity was developed with the help of Colin Osborne.

## **Credits**

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Health & safety checked May 2018

Page last updated October 2018