Thermal anomaly of water

Aims of the experiment

- To verify the thermal anomaly of water by determining a density maximum
- To measure the height of capillary rise of water at various temperatures in a vessel with a capillary
- To derive a formula for the relationship between the height of capillary rise in a vessel and the density of the liquid.
- To explain the anomalous density of water using its molecular structure.

Principles

Most substances expand when they are heated. In other words, the density of the substances decreases as the temperature increases. The reason for this is the increasing motion of the individual molecules as the temperature rises, which in turn results in an increase in the distance between the particles.

Some materials behave differently to this general behaviour. This is called anomalous density. Materials with anomalous density expand above and below a certain temperature. This temperature is called the density maximum.

The most important anomalous density for our lives is that of water, since without this anomalous density, the oceans of our planet would probably freeze. Pure water has a density maximum of about 4 °C. Liquid water at a temperature of 4°C therefore has a higher density than liquid water at a temperature near the freezing point. In winter, a temperature gradient forms with the 4 °C cold water being located below and the colder water being located above. A waterway will therefore always freeze from the top down. Since the ice cover acts as an insulator, a waterway will freeze only slowly, and usually not completely, so a liquid layer is located below the ice in which water-borne life forms can survive.

The cause of the anomalous density of water is hydrogen bonding. Water is a dipole molecule with an angled structure. The two hydrogen molecules have a positive partial charge, and the oxygen is partially negatively charged. Since opposite charges attract and the same charges oppose one another, the negatively charged oxygen atoms align with the positively charged hydrogen atoms of adjacent molecules. In the solid aggregated state, when molecular motions are minimal, a rigid crystal matrix forms in which one oxygen atom is tetrahedrally coordinated with 4 hydrogen atoms and vice versa one hydrogen atom with 4 oxygen atoms. The resulting structure makes minimal use of space, and there are open gaps between the atoms. As molecular motion increases, this rigid arrangement is dissolved in favour of increasingly flexible structures in which hydrogen bonds to adjacent molecules continue to form, but where water molecules fit into the gaps. This means that these structures are making better use of space than the rigid crystal matrix. This increases the density. In the process, there is a continuous transition which continues even in the liquid state up to a temperature of 3.983 °C. Beginning at this temperature, the increasingly strong molecular motions lead to higher separations between the molecules than is the case for most other materials.

Fig. 1: Set-up of the experiment

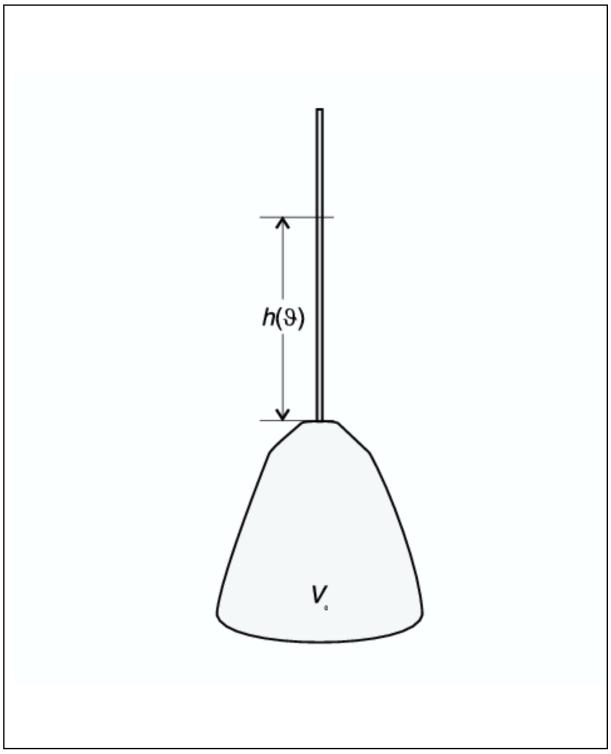

Fig. 2: Schematic illustration of the apparatus.

In this experiment, the density maximum of water is determined by measuring the volume change in a vessel using a capillary (see Fig. 2). The experimental apparatus is cooled starting from room temperature and in the process the vertical height *h* of the water level is continuously determined as a function of temperature. Using a literature value for the density *ρ* of water at the starting temperature of 15 °C, the densities at the respective temperatures can be calculated using the measured vertical heights. The following relationship between the density relationships and the volume relationships at the various temperatures can be used for this:

$$\frac{\rho(T_1)}{\rho(T_2)} = \frac{\frac{m}{V_1}}{\frac{m}{V_2}} = \frac{\frac{1}{V_1}}{\frac{1}{V_2}} = \frac{V_2}{V_1}$$

The total volume of the vessel at the respective temperatures can be calculated using the vertical heights:

$$V(T) = V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T)$$

V_0 is the volume of the glass vessel. d^2 is the internal diameter of the capillary.

d = 0.2 cm

V_0 = 310 ml = 310 cm^3

When this formula is put into the equation above, we have:

$$\frac{\rho(T_1)}{\rho(T_2)} = \frac{V_2}{V_1} = \frac{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T_2)}{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T_1)}$$

For density *ρ* of T_1, what we find is therefore:

$$\rho(T_1) = \frac{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T_2)}{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T_1)} \cdot \ \rho(T_2)$$

Risk assessment

The measurement should be discontinued before reaching 0 °C for safety reasons since the apparatus can become damaged due to the abrupt expansion of water upon freezing.

Equipment and chemicals

1	Stand rod, 60 cm, 12 mm diam.	608 040
1	Stand rod, 47 cm, 12 mm diam.	300 42
3	Bosshead clamp S	301 09
3	Universal clamp 0...80 mm	666 555
2	Stand base, V-shaped, small	300 02
1	Funnel, PP, 75 mm diam.	665 009
1	Tubing 8 mm diam. 1 m, rubber	307 66
1	Anomaly of water apparatus	667 505
1	Protective sleeves for temperature probe	666 194
1	Stirring magnet, 25 mm x 12 mm diam.	604 590
1	Magnetic stirrer	666 8451
1	Temperature probe, NiCr-Ni, 1.5 mm	529 676
1	Universal Measuring Instrument Chemistry	531 836
1	Laboratory dish, Boro, 140 x 75 mm Ø	602 725
1	Beaker, Boro 3.3, 400 ml, tall	602 011
1	Spoon-ended spatula, 180 mm	666 966
1	Electronic balance, 1000 g : 0.1 g	ADACB1001
1	Pipetting ball (Peleus ball)	666 003
1	Sodium chloride, 250 g	673 5700
1	Distilled water	675 3400

Additionally required:
- Waterproof pencil
- Crushed Ice
- Ruler (30 cm)

Set-up and preparation of the experiment

1. First, set up the two stands by screwing the stand rods into the stand bases provided. Attach the funnel to a bosshead and a universal clamp at about 55 cm of height. Shorten the 8 mm diameter tubing to 50 cm in length and pull it over the opening of the funnel.

2. Place the water anomaly measuring apparatus on a magnetic stirrer. The GL closures are first unscrewed. Put in a stirring magnet.

3. Place the temperature sensor into a protective tube and screw it into the lateral opening of the water anomaly measuring apparatus using a GL screw cap. Prepare the Universal Measuring Instrument Chemistry and insert the temperature sensor into the Type K inlet.

4. Connect the tube connected to the funnel to the apparatus. Add distilled water until the upper edge of the upper opening is reached. Remove air bubbles by swirling the device.

5. Then, screw the capillary into the apparatus using a GL screw cap so that it extends about 1 cm into the apparatus.

Note: If the GL screw cap is not screwed on, the capillary *can be pushed loosely through the gasket. But the* capillary *is fixed as soon as the GL screw cap is tightened.*

6. The funnel is refilled with distilled water and the valve is opened until the upper edge of the capillary is reached.

Note: Air bubbles should be avoided here as well. If it doesn't work the first time, the capillary *can be removed and the air bubbles suctioned out using a pipetting ball.*

7. Prepare the freezing mixture. To do so, weigh out 300 g of crushed ice on the laboratory dish, add 26 g of sodium chloride and stir with the spatula. The cooling works best when using as small pieces of ice as possible and with

good mixing with the salt. If necessary, keep a bit more ice ready to add.

Performing the experiment

1. Turn on the Universal Measuring Instrument Chemistry.

2. When the temperature is correctly displayed (room temperature), the device for measuring the thermal anomaly is placed into the freezing mixture on the magnetic stirrer and fixed there using the second stand. A universal clamp and a bosshead are used to fix the device and another set to fix the temperature sensor.

3. Immediately after adjusting the device in the water bath, the magnetic stirrer is turned on.

4. Wait until a temperature of 15 °C is reached. Then, the starting point of the measurement is marked using a waterproof pencil on the capillary.

5. From this point on, the decrease or increase in liquid level is measured and recorded in temperature steps of 0.5 °C.

6. The measurement is continued until a temperature as close to 0 °C is reached (from 2 down to 0.5 °C is sufficient).

Caution: Since water expands suddenly during freezing, the apparatus can be damaged. The apparatus should therefore be removed from the freezing mixture before reaching 0 °C for safety reasons.

7. After the measurement is completed, the capillary is removed and the height of the start value previously marked at 15 °C is measured.

Observation

1. The liquid level drops noticeably before reaching the starting temperature of 15 °C.

2. The interval between measurements decreases at constant temperature intervals.

3. The liquid level continues to drop until a temperature of about 4 °C is reached.

4. Then, the liquid level increases again and the intervals between the measurements increase.

All measurements are listed in Table 1.

Evaluation

The values recorded are relative heights compared to the starting value. The starting value is added to these relative heights in order to obtain absolute heights. The starting value can vary depending on the room temperature and on the level prior to cooling down to 15° C, and should be between about 15 and 25 cm. In this example measurement (see Tab.1), the starting value is 21.8 cm

The absolute heights obtained through this method are used as $h(T_1)$ in the formula for calculating the density. As a reference value for the density, a literature value for the density of pure water at 15 °C is used:

$\rho_{Water}(15\ °C) = \rho(T_2) = 999.1\ g\ l^{-1}$

Tab. 1: Example measurement of anomalous density. The reference value for ρ(15 °C) is marked.

T [°C]	h_{rel} / cm	h / cm	ρ / g l^{-1}
15	0	21.8	***999.1***
14.5	-0.7	21.1	999.38
14	-1.5	20.3	999.70
13.5	-2.2	19.6	999.99
13	-2.8	19	1000.23
12.5	-3.5	18.3	1000.51
12	-4.1	17.7	1000.75
11.5	-4.9	16.9	1001.07
11	-5.2	16.6	1001.19
10.5	-5.7	16.1	1001.40
10	-6.2	15.6	1001.60
9.5	-6.7	15.1	1001.80
9	-7	14.8	1001.92
8.5	-7.4	14.4	1002.08
8	-7.7	14.1	1002.21
7.5	-7.9	13.9	1002.29
7	-8.2	13.6	1002.41
6.5	-8.3	13.5	1002.45
6	-8.5	13.3	1002.53
5.5	-8.5	13.3	1002.53
5	-8.6	13.2	1002.57
4.5	-8.6	13.2	1002.57
4	-8.6	13.2	1002.57
3.5	-8.5	13.3	1002.53
3	-8.4	13.4	1002.49
2.5	-8.2	13.6	1002.41
2	-8.1	13.7	1002.37

For h(T_2), the starting value of T = 15 °C is used. In this example, $h(T_2)$ = 21.8 cm.

The inside diameter d of the capillary is 0.2 cm.

V_0 is the internal volume of the measuring apparatus without capillary and is about 310 ml = 310 cm³.

$$\rho(T_1) = \frac{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T_1)}{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T_2)} \cdot \rho(T_2)$$

$$= \frac{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(T_1)}{V_0 + \pi \cdot \frac{d^2}{4} \cdot h(15\ °C)} \cdot \rho(15\ °C)$$

$$= \frac{310\ \mathrm{cm}^3 + \pi \cdot \frac{0{,}2^2}{4} \cdot h(T_1)}{310\ \mathrm{cm}^3 + \pi \cdot \frac{0{,}2^2}{4} \cdot 21{,}8\ \mathrm{cm}} \cdot 999.1\ \mathrm{g\ l^{-1}}$$

For the first measurement at 14.5 °C, the following is:

$$= \frac{310\ \mathrm{cm}^3 + \pi \cdot \frac{0{,}2^2}{4} \cdot 21.1\ \mathrm{cm}}{310\ \mathrm{cm}^3 + \pi \cdot \frac{0{,}2^2}{4} \cdot 21.8\ \mathrm{cm}} \cdot 999{,}1\ \mathrm{g\ l^{-1}} = 999.39\ \mathrm{g\ l^{-1}}$$

The calculated values for the density are plotted in a spreadsheet program versus the temperature and a polynomial trend line is added. The function of the trend line can be displayed in the diagram (see Fig. 3). The density maximum corresponds to the maximum of the function. It is determined by calculating the first derivative and determining null.

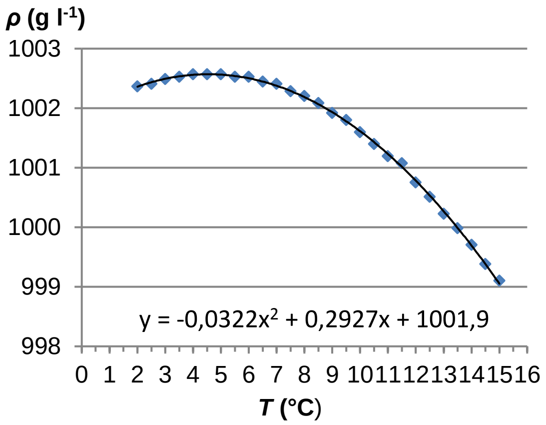

Fig. 3: Determining the density maximum. To do this, the density calculated from the vertical height is plotted against the temperature. The formula of the polynomial trend line is indicated.

The first derivative of the trend line function in Figure 3 is:

$$y = -0.0664x + 0.0297$$

For the first derivative, null corresponds to the maximum value of the function.

$0 = -0.0664x + 0.0297$

$0.0297 = -0.0664x$

$4.545 = x$

From the data in this example measurement, a density maximum for water occurs at $T = 4.6$ °C.

Using this temperature in the equation for the trend line function, the maximum density is:

$-0.0322 \cdot (4.545)^2 + 0.2927 \cdot (4.545) + 1001.9 = 1002.57$

$\rho = 1002.57$ g l^{-1}

Results

In Figure 3, it can be seen that water exhibits anomalous density. The graph shows the typical shape of a density temperature curve of a material with anomalous density. The density maximum lies between 3.5 and 5.5 °C.

In the literature, a temperature of 3.983 °C is given for the density maximum of pure water. The density of water at this temperature is 999.98 g l^{-1}. The value calculated for the temperature of the density maximum using this example measurement, which is T = 4.6 °C, deviates from this value. The calculated maximum density, $\rho = 1002.57$ g l^{-1}, is also above the literature value. Overall, the calculated densities are somewhat higher than the values given in the literature for pure water.

It must be noted that the literature values are given for absolutely pure water. In this experimental arrangement, distilled water was used. However, this still contains some dissolved gases which can have an effect on the density or measured volumes at a specific temperature. Another influencing factor is the low precision of taking readings from the capillary which does not allow more accurate readings in the range from 4 to 5 °C.

Cleaning and disposal

The freezing mixture with the ice and salt can be disposed of in the sink.