Figure 1: Temperature of water versus time. Experimental results for $0.2kg$ of water heated by a gas heater in a pot without a lid.

Figure 2: Temperature of water versus time. Experimental results for $0.2kg$ of water heated by an electric heater in a pot without a lid.

Figure 3: Time dependence of temperature calculated on a basis of the theoretical model for a pot without a lid ($m = 0.2kg$)

Figure 4: Time dependence of temperature calculated on a basis of the theoretical model for a pot with a lid ($m = 0.2kg$)

prob3.tex **Problem 3**

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Drop

The task was to explain a phenomenon of arising a system of rings when drying up a drop of salted water. An experiment was carried out to investigate this problem. It consisted of a number of smaller experiments in which drops of salted water were dried up under different conditions. Following factors were taken in consideration when preparing experiments:

1. Temperature of the environment (a quantity of energy supplied in the unit of time).
2. Salt concentration in the solution.
3. Shape (intersection) of the drop, connected with the texture of the surface.

To check the influence of the environment temperature on ring formation, we carried out experiments at different temperatures: (i) room temperature, (ii) heating with $40W$ white-light lamp, (iii) heating with $400W$ red-light lamp. It was not necessery to know the exact temperature in each of experiments and it was not checked. These experiments were performed only to determine whether different temperatures alter the shape or the mechanism of ring formation. No influence was noticed. The change of the temperature modified only the speed of a whole process. Lamps were used as heaters to achieve identical temperature of both base surface and the air around the drop. Of course, the measurements were carried out only in temperatures between $0°C$ and $100°C$. As for the temperatures below $0°C$, the reason is clear. If the surface on which the drop lays is warmer than $100°C$, a narrow layer of steam arises between the drop and the surface which both prolongs the process and makes formation of rings impossible.

The most important factor in the whole experiment was the concentration of salt in the solution. We used following concentrations: $320g/l$, $160g/l$ and $80g/l$ (approximate values). The temperature of the environment (and of water) had very little influence on solubility of salt because the dependence of natrium chloride solubility on temperature is very weak (in comparisson with other salts) and ranges from $360g/l$ for $0°C$ to $400g/l$ for $100°C$. We additionaly used samples of supersaturated solution and samples with very low salt concentration (so low that the measurement error of the concentration was comparable with its value).

An expression "smooth surface" was used in the problem. It was not told of what material that surface should be. Different surfaces have different values of surface interfacial tension. Besides, they may differ in texture, and what for us may seem ”smooth” in fact may be uneven and irregular. But whatever the surface is, it may change only one thing, the shape of the intersection of the drop. It can be very flat (for instance due to small boundary angle), or bulged (when boundary angle is bigger). The shape of the intersection depends also on the size of the drop (precisely: on the ratio of a diameter of the drop to its thickness). A boundary angle influences mainly this part of drop which is closer to its rim. For wider drops their middle part is almost flat. Experiments were carried out for drops with various sizes (from about $2mm$ up to $3cm$ diameter) and on surfaces with different boundary angles (Fig. 1).

Figure 5: Intersections of drops

In our experiments we obtained rings for all the samples. They were bigger for high concentrations of salt in a solution and for big boundary angles — both factors had influence on the height of the ring's wall. For very flat drops and for low concentrations the rings were visible, but their height was very low (non-measurable). For mostly bulged drops the height of the rings was up to $2mm$. The shape of their intersection was hollow (Fig. 2). It was easy to notice for all the rings that they consisted of a number of big natrium chloride monocrystals bounded to each other with fine salt structures.

There were small monocrystals spread inside the rings (Fig. 3). For low value of a boundary angle the main ring was not continuous. It consisted of big monocrystals as in other cases, but they were

Figure 6: Shape of a ring

Figure 7: View of a ring

separated. There was wide flat ”swelling” of salt visible around the main ring which flew through slits between the monocrystals. It created a complex structure of small channels that became visible after dropping some dye on the swelling. The shape and direction of the channels indicated how the outer ring of swellings had been formed. (Fig. 4). For small concentration and low boundary angle the width of the swelling was up to $8mm$, but when the concentration of the solution was higher and the main ring more thick and continuous, the outer swelling was no wider than $1mm$.

The most complex is, of course, the formation mechanism of the main ring. It was explained thanks to experiment in which the solution was supersaturated. Salt was diluted in hot water. After this a drop was created in colder environment (both surface and air had lower temperature than the water). Thus the solution was all the time supersaturated while the drop was drying up and the salt

Figure 8: Border area of a drop

was precipitating. We observed the whole process. Extremely small monocrystals of salt were precipitated from the drop. Almost all of them arose on the drop surface, where most of the evaporation took place. They were very light and therefore they did not fall to the bottom of the drop, but were kept up on its surface by surface tension. There, where surface of the drop was more inclined (closer to the edges), monocrystals were flowing down the surface to the rim of the drop (still kept up by the surface tension) to create the ring (Fig. 5).

Figure 9: Formation of a ring

When the process took place, monocrystals grew larger while new Na^+ and Cl^- ions joined them. That is why not all of the monocrystals got to the ring. Some of them appeared to be too heavy for surface tension to hold them. They fell down the drop to the bottom creating monocrystals later seen inside the ring. This process also answers, why the shape of the ring for higher boundary angles was hollow. The monocrystals flowing down the surface, when joining the ring were still held by surface tension. That is why the shape of the intersection of the ring is the same as the initial shape of the drop.

The mechanism of ring formation is, of course, the same for lower salt concentrations. In other cases, when we illuminated the surface of the drop when looking at it from different angles, we could see small reflects of the light on its surface. We can be sure that it was light reflected from the walls of monocrystals too small to be seen, but big enough to give distinct sparkle.

For very small salt concentration we were able to see another process. When the amount of salt in water was so small that it hardly created the main ring, we could see another ring formation. When the ring is being formed, salt water sticks to the ring. When some water evaporates, the drop has a tendency to decrease its diameter and to get smaller. If there are already some precipitated monocrystals inside the ring, the drop draws back clutching to these crystals until it finally dries up. But if the concentration is so low that there are no monocrystals inside the ring at all and the surface of the bottom is completely flat, the drop has nothing to clutch to, while it dries up for some time, it still holds to the outer ring that it created. But when it gets too flat, its surface tension draws the drop back, puts it together and tears off the outer ring. The drop finds itself inside the ring that has been just created in the same situation as it was at the beginning. The boundary angle is again characteristic for the interface drop – surface. The intersection of the drop is similar to that from the beginning of the process. The only difference is that the amount of the solution in the drop is smaller. The whole process starts again. Another ring is being formed. The whole process may repeat a few times and create a system of rings which are situated one inside another. However such situation may appear only, when the concentration of the solution is not too high.