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The Soret Effect Reversed

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NOTE

The Soret Effect Reversed

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In an attempt to set up a simple laboratory experiment for illustrating and assessing thermal diffusion in solutions we were surprised to find that, owing to the arrangement used, the solute became more concentrated at the hot end instead of at the cold end as is almost always the case. However, once again it turns out that what appears to be a negative result can serve a useful purpose.

The intended experiment was planned as follows. The top of a large aluminum cylinder (3.5 × 3.5 in.), cooled in an ice/water bath, provided the cold temperature. The top surface of the block was coated with epoxy resin to render it inert and then with silicone grease to make it water-repellent; on top was placed a stack of five filter papers (#1 or #541 Whatman) or, even better, glass fiber filters (Reeve-Angel). The latter material was preferred because it was found to be more absorbent and had a more uniform capacity for holding liquid in that the top paper in the stack was found to hold as much liquid as the bottom one. The solution to be studied was allowed to soak into the stack of papers until they were just full. A petri dish cover was then placed over the stack and an infrared lamp used as the source of heat on the top surface.

Because the solution was immobilized in the pores of the paper, convection presented no problem, and at the end of the experiment the separation achieved was found by separating the filter papers and either dissolving and analyzing each separately or, in cases of certain solutes, by simply evaporating off the water from the solute and weighing the filter paper plus dry solute, having also determined the mass of the dry paper itself. Results from one such determination on a

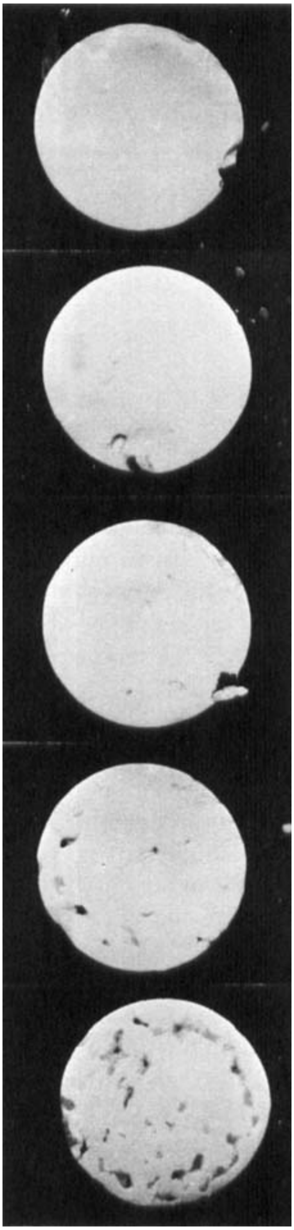

FIG. 1.

solution of cadmium sulfate 0.05 molal showed the following distribution of masses of solute, in grams, in the papers from top to bottom respectively: 0.0842, 0.0308, 0.0111, 0.0043, and 0.0019.

When a concentrated solution of potassium chloride (approximately 3 M) was used in the experiment it was found that the top three papers were so saturated with salt that they adhered to each other and to the dish. In order to give visual indication of distribution of solute, a solution of copper sulfate (80 g per liter) was used. Saturation was again exceeded and blue crystals appeared in the upper papers. More than half the solute was eventually crystallized in the top paper, while the bottom paper contained almost pure water. The effect is illustrated in Fig. 1, which has the top paper on the left.

The effects obtained are, of course, much more drastic in extent than the Soret effect, and reversed in sense with concentration of solute occurring at the hot end. What makes this cell unsuitable for Soret measurements is the presence of an air space that connects the top and bottom regions of the cell. This "greenhouse" condition, with the lamp shining through the petri dish onto the top paper, causes water to evaporate at the top and condense in the coolest place at the bottom, where the condensate soaks into the bottom paper by capillary action and then up the stack of papers, completing an evaporating-condensation-capillary cycle that amounts to a distillation process with total reflux. By the above cycle the condensate sweeps solute up the stack to the top where it may crystallize out, and leave almost pure water at the bottom; the relatively small tendency for Soret separation in the reverse direction is swamped.

The results described above can be applied in at least two situations. First, the experiment suggests the possibility of separating salt from water, or both from sea water. Such an experiment was tried using sunshine from above through fiber glass and cold water below to provide the temperature gradient and with sand replacing the filter papers as the capillary material. Separation was achieved at little cost but the proper design of such equipment, especially on a large scale, is considered outside the present scope, especially since no novel operations are involved.

The second point concerns a clarification of troubles experienced by various workers doing Soret experiments with vapor present in the cell. Under such conditions results have sometimes been described as unpredictable and occasionally as reversed in sense. On the other hand, owing to the virtual incompressibility of liquid solutions, it is not convenient to arrange for a cell to be completely full of liquid and, without leaking, to withstand any change in temperature. From the present report it can be seen that a vapor space will only be destructive if it connects the top and bottom regions of the cell so that the cyclic evaporation–capillary process occurs. A small vapor space only at the center of the cell, or perhaps at the top only, and where filling is carried out, should not allow the cyclic process to develop. Rather, such a small vapor space can advantageously serve as a small cushion for expansion effects owing to changes in temperature.

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