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Precision Measurements of the Thermal Conductivities of certain Liquids using the Hot Wire Method

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Experiments have been performed on water, glycerol and aqueous solutions of glycerol, ethyl alcohol and sucrose. In these experiments, no convection was observed during a determination when it was carried out at the temperature of maximum density. But it was found that the further the experimental temperature was from this temperature of maximum density, the earlier the convection started. However, using the experimental readings obtained before convection began, it was possible to calculate the thermal conductivity without any loss of accuracy. Accurate experiments have in this way been performed up to 20° C. The electrically heated wire was always placed vertically so as to minimize convection — it was found that the greater the angle between the wire and the vertical, the sooner the convection began. The method gave an automatic indication of the presence of convection, thus making possible the determination of suitable conditions for precision measurements. The high accuracy, of which this method is capable, is obtainable for highly viscous liquids but is otherwise limited to fluids of low thermal dilatation.

Using the method described in the previous article [1], the thermal conductivities of various liquids and solutions were determined and, in addition, the influence of convection on measurements of this type was investigated. The convection effect can be considered in the following manner. During the first instants of the experiment when convection has not had time to be effective, a straight x *versus* log t curve will be obtained whose slope is determined by the value of the thermal conductivity (and hence the k log t—x *versus* x curve will be a straight horizontal line) where x is the galvanometer scale reading, t the time and k the slope of the x *versus* log t graph (*cf.* Figs. 6 and 7 in Ref.[1]). When convection begins, heat will be lost quicker from the central heating wire because cooler liquid will be moving up to the wire by convection. Thus the thermal conductivity will appear to be greater and the k log t—x graph will curve upwards.

However, if the cell is placed vertical, convection should initially take place in concentric cylindrical surfaces and the convection effect should therefore be less than in any other case. For example, a typical experiment on a 4.9 % solution of sucrose in water gave the following graph, Fig. 1. The measurement was performed at 4.0° C, near the density maximum of the solution where the thermal dilatation is small.

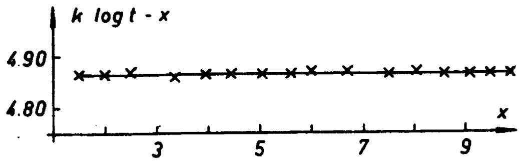

Fig. 1. k log t—x versus x (the galvanometer scale reading) for a 4.9 % aqueous sucrose solution. k = 8.71. Temp: 4.0° C, Cell: placed vertical, I = 0.28 amp (the heating current).

The straightness of the graph indicates the absence of convection. The value calculated for the thermal conductivity was $\lambda = 0.001328$. However, when the cell was placed at an angle of 45° to the vertical, the graph in Fig. 2 was obtained:

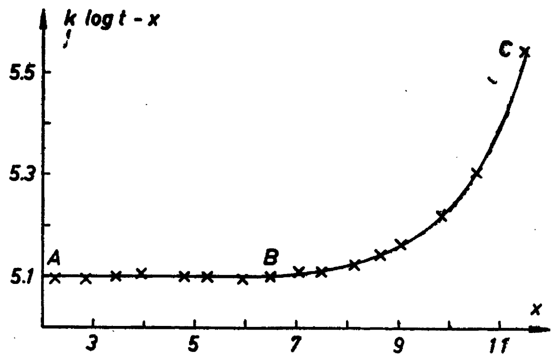

Fig. 2. k log t—x versus x for same solution as in Fig. 1. k = 10.17. Temp: 4.0° C, Cell: 45° to the vertical, I = 0.28 amp, AB: convection—free period, BC: effect of convection.

Convection began at the point B after 14 sec. (The total time from A to C was, for all determinations, about 60 sec.) In an experiment in which the convection effect is greater, the point B will occur earlier during the experiment and the deviation of the BC section from the horizontal will be larger. However, it should be possible to calculate the thermal conductivity from the initial section, AB. A value, $\lambda = 0.001330$, was obtained from the AB section in close agreement with the value calculated from Fig. 1. This shows that, if convection did occur in an experiment and a curved $k \log t—x$ graph was obtained, it was still possible to calculate an accurate value for the thermal conductivity using the initial, straight portion of the graph. Apart from several further experiments carried out to check this important conclusion, the cell was always placed vertically so as to minimize convection from this source.

However, there are various other factors which must be taken into account. Firstly, convection will be influenced by the effect of the solute on the viscosity of the solvent. Secondly, convection will be at a minimum at the temperature of maximum density (t.m.d.) and that is why convection was not apparent during the experiments, carried out at 4° C, on the less concentrated aqueous solutions. However, an increase in the concentration results in a decrease of the t.m.d. and should hence give rise to a larger convection effect if the experiment is performed at the t.m.d. of pure water. This explains the occurrence of convection in the experiments on the more concentrated solutions carried out at 4° C.

With glycerol/water mixtures for example, it was found that the convection effect (as judged by the k log t—x graph) increased with increasing glycerol concentration until such a concentration was reached at which the properties of the glycerol became more dominant and that then, because of the high viscosity of solutions containing a high percentage of glycerol, the convection effect decreased as the concentration increased to 100 %. In all cases studied, however, it was possible to calculate the thermal conductivity from the initial, straight portion of the k log t—x graph.

With distilled water at 4° C, no convection was detected both when the cell was vertical and when it was placed at an angle of 45° to the vertical. This shows that the convection arising from a 45° inclined heating wire, under these conditions, is negligible at the t.m.d. However, with water at 20° C and the cell placed vertically, convection began as soon as 20 sec (point E) after the heating current was switched on (Fig. 3).

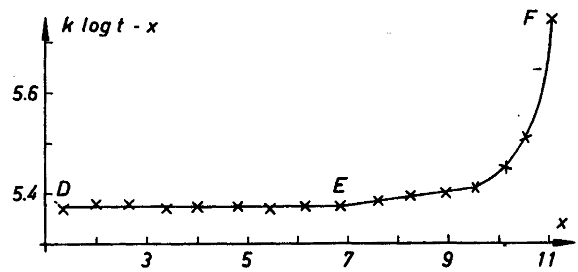

Fig. 3. k log $t-x$ versus x for water. k = 9.47. Temp.: 20.0° C, Cell: placed vertical, I = 0.27 amp. DE: convection-free period, EF: effect of convection.

The thermal conductivity calculated from the DE section was 0.001442.

RESULTS

The measurements are summarized in Table 1. Each value is a mean of up to 8 independent determinations.

Table 1.

Medium	Concentration (weight %)	Current (amp)	Thermal conductivity λ	Convection appeared after	Temp. (° C)
Solution of glycerol in water	4.94 16.00 31.06 63.50 95.24	0.28 0.27 0.27 0.28 0.28	0.00131_7 0.00123_0 0.00111_9 0.00087_0 0.00069_2	20 sec 19 sec 22 sec — —	4.0 4.0 4.0 4.0 4.0
Solution of ethyl alcohol in water	4.0 14.15 28.9	0.28 0.28 0.28	0.00129_0 0.00114_9 0.00096_8	— 50 sec 20 sec	4.0 4.0 4.0
Solution of sucrose in water	4.9 15.5 24.75	0.28 0.28 0.28	0.00133_0 0.00126_3 0.00119_8	— — —	4.0 4.0 4.0
Water »		0.27 and 0.32 0.27	0.00135_4 0.00144_2	— 20 sec	4.0 20.0
Glycerol »		0.27 0.27 and 0.21	0.00067_9 0.00067_5	— —	4.0 20.0

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