

A flow calorimeter for enthalpies of mixing The enthalpy of mixing of *n*-hexane + cyclohexane at 298.15 K

M. L. McGLASHAN and H. F. STOECKLI

Department of Chemistry, The University, Exeter, U.K.

A new flow calorimeter for measurements of enthalpies of mixing is described. It has been used to make a series of measurements on *n*-hexane + cyclohexane at 298.15 K with a view to recommending that pair of liquids for checking new calorimeters. The results, including the present ones, obtained as the result of an international cooperative effort in five different laboratories with five quite different calorimeters, reveal no systematic discrepancies and establish the enthalpy of mixing at 298.15 K with a certainty unprecedented in this field. A few measurements have also been made at 313.15 K.

1. Introduction and scope

We have little doubt that thermometrically undisclosed heat leaks are an important source of the discrepancies⁽¹⁾ which, in spite of recent advances,⁽²⁻⁶⁾ are still found among measurements of enthalpies of mixing made in "static" calorimeters. With a flow calorimeter it is possible, by varying the flow rates, to eliminate errors caused by heat leaks. When we began to build a flow calorimeter for enthalpies of mixing the only one which had been described in the literature was that of Rose and Storvick.⁽⁷⁾ Since then Sturtevant and Lyons⁽⁸⁾ have also described one. We believe that the one described below is a more accurate instrument than either of the previous ones. It is not yet, however, capable of the reproducibility which we⁽⁹⁾ and others^(2-6, 10, 11) have been able to achieve with static calorimeters. Nevertheless we believe that improvements in design and measurement will eventually lead to flow calorimeters which supersede static calorimeters in this field.

As part of an international effort,^(5, 8, 10, 11) arranged by one of us (M.L.M.) for the I.U.P.A.C. Commission on Thermodynamics and Thermochemistry, to find a pair of liquids for which the enthalpy of mixing was sufficiently well established by concordant measurements made in several different calorimeters and in several different laboratories, so that it might be recommended for testing new calorimeters, we have used our flow calorimeter to measure the enthalpy of mixing of the chosen pair of liquids *n*-hexane + cyclohexane at 298.15 K. We have also made a few measurements at 313.15 K so as to obtain a value of the temperature coefficient of the enthalpy of mixing sufficiently accurate for the correction to 298.15 K of measurements made close to but not at that temperature.

