ELSEVIER

Thermochimica Acta 289 (1996) 367–369

thermochimica
acta

Hysteresis in the determination of the heat-loss number

Enio Kumpinsky

R&D Department, Ashland Chemical Company, PO Box 2219, Columbus, OH 43216, USA

Received 4 December 1995; accepted 6 March 1996

Abstract

The heat-loss number is a dimensionless group that accounts for heat losses in the evaluation of calorimetric experiments. It is obtained with steady-state measurements at various temperatures in the range of interest. It was established that this parameter is highly dependent on the direction of temperature variation, which affects the amount of condensate on the walls. Most of the condensate is formed at the highest temperature during the test and it acts as insulation. Upon heating and then cooling, the heat loss number is significantly higher when the temperature is raised than when it is lowered, if the reactor is dry prior to the test. When the reactor walls are wet or the directions are reversed, i.e., cooling and then heating, there is no significant hysteresis, because the reactor walls are saturated with condensate in either direction.

Keywords: Calorimeter; Heat loss; Heat transfer; Hysteresis; Temperature

1. Background

In another publication in this issue of Thermochimica Acta [1], we indicated how the heat-loss number can be used to interpret reaction calorimetry data. It was shown by means of examples that this dimensionless group improves the accuracy of heat-flow calculations. We demonstrated that the heat-loss number can be determined with experimental data only, for a particular set of operating conditions. To obtain N_α (see Nomenclature in Ref. [1]), the system is stabilized at different temperatures by raising and lowering the T_r setpoint. The experimental points are then fitted to a parametric equation with a structure that makes physical sense. For example, if heat losses by vaporization are dominant, the three-parameter Antoine equation might be preferred. This correlation is used with other calorimetric data to yield the heat flow of a chemical or physical process.

0040-6031/96/$15.00 © 1996 – Elsevier Science B.V. All rights reserved

PII S0040-6031(96)03008-0

2. Experimental method

The instrument of this work is the RC1 Reaction Calorimeter, manufactured by Mettler Toledo, equipped with the AP01 glass atmospheric pressure reactor [2], having an anchor agitator turning at 100 rpm. The reactor, initially dry, was charged with 1.208 kg of water, for a wetted surface area of 0.0531 m^2. The temperature in the surroundings was 22°C. T_r was raised in 10°C increments beginning at 30°C, with a stabilization period of 45 ± 15 min. The exception was 99°C instead of 100°C, to avoid boiling. After that, the temperature was lowered and stabilized at 90°C and at 10°C decrements, ending at 30°C. The heating step was then repeated, except that the walls in the vapor space were saturated with condensate as a result of the previously held higher temperatures.

3. Discussion and conclusion

Using Eq. (7) of Ref. [1], $N_\alpha = \alpha/UA = (T_a - T_r)/(T_r - T_{amb})$, with data from the stabilized temperature setpoints, we obtained the graph of Fig. 1 . The hysteresis of the heat-loss number is clearly noticeable. When T_r was increased for the first time, especially at lower temperatures, there was almost no water condensate on the reactor walls of the vapor space. As the temperature was raised, more condensate deposited on the walls. When the temperature was lowered from 99°C, the condensate remained on the walls. It formed an insulating barrier that reduced heat losses, resulting in a significantly lower value of the heat-loss number. When T_r was increased for the second time, the reactor walls of the vapor space were already saturated with water

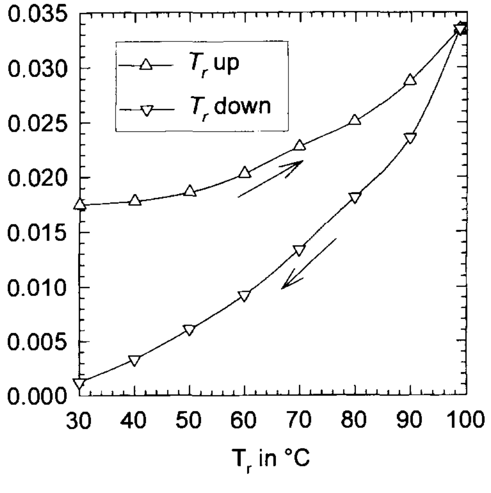

Fig. 1. Example of hysteresis of the heat-loss number.

condensate. Consequently, the insulating effect of the condensate was discernible from the beginning. N_α for the second temperature rise coincided with the T_r down curve in Fig. 1, and it was not plotted. Before performing tests to yield the heat-loss number, it is essential to consider the conditions of the system that will undergo a chemical or physical process. Knowing that the insulating effect of the condensate can have a marked effect on the heat-transfer calculations, the direction of temperature variation and maximum T_r should be carefully weighed for the N_α experiments.

References

[1] E. Kumpinsky, A method to determine heat-transfer coefficients in a reaction calorimeter, Thermochim. Acta, 289 (1996) 351–366.

[2] Mettler Toledo RC1*e* Reaction Calorimeter Operating Instructions, Switzerland, November 1995, Chap.2 and 3.