Determination of Partial Molar Enthalpies by Adiabatic Calorimetry

INTRODUCTION

- The objective of this experiment is to demonstrate the enthalpy change in mixing phenomena for binary solutions. Accurate determination of heat of mixing will be undertaken using an adiabatic calorimeter and thereby calculating partial molar enthalpies of the components and heat capacities of pure solvents and solutions.

- Calorimetry is the science of measuring the heat of chemical reactions or physical changes. It involves measurements of enthalpy changes in various processes like mixing, dilution, dissolution, absorption or crystallization. It is performed using a calorimeter. In adiabatic calorimeter, there is no heat flow to or from surroundings and temperature is the monitored variable in the process. Accuracy of experiment depends on accurate measurement of temperature and good adiabatic shielding.

SCHEMATIC DIAGRAM OF APPARATUS

Fig: Adiabatic Calorimeter

D = Dewar Flask of capacity 150 ml,
S = Polypropylene Stopper, H = Resistance Heater,
ST= Stirrer, T = Temperature Sensor
QUESTIONS

Perform the experiment to test the following hypotheses:

1. The calorimeter functions adiabatically
2. A temperature increase of 2°C is sufficient to estimate “K” with < 5% uncertainty. Uncertainty decreases if dynamic std-dev is used instead of least count.
3. For a given 2-component system mixing can only be an exothermic or endothermic process.
4. Find the heat capacity of the pure component along with its uncertainty. Compare with literature value and comment.
5. Find the partial molar enthalpy of mixing at x1=x2=0.5 and at infinite dilution.

METHODS

MEASUREMENTS

Students have to choose what variables (dependent or independent) to measure. For example: The independent variables can be any of these - time, voltage, mass of solution, initial temperature, final temperature and dependent variables can be current, K, C_p, Δh_m.

UNCERTAINTY IN MEASURED VARIABLES

Students need to determine the static uncertainties for the equipment using the least count of the instruments and dynamic uncertainties making multiple measurements.

CALCULATION AND PLOTS

Students need to measure the data relevant to the hypothesis given to them and plot the respective graphs, in order to test the hypothesis.

INTERPRETATION

Based on the findings, students should state whether the hypothesis was proved to be true or false, and give suitable reasons for the same.

CALCULATION PROCEDURE

(1) To find water-equivalent of calorimeter:

Since the various parts such as stirrer, heater, temperature sensor, stopper and walls of the ask absorb some heat it is necessary to know the calorimeter water-equivalent, K. For this purpose a known amount of heat, $Q$ (Joules) is supplied to the calorimeter containing (say) $m$ gm of water of heat capacity ($C_p$ (J/g K)). If $ΔT$ is the observed temperature change, then:

$$Q = mC_p ΔT + K ΔT \quad (i)$$
Hence $K$ can be calculated from equation (i), the other quantities being known experimentally.

(2) To find heat capacity of a pure liquid or a solution:

As shown in Figure (see Theory), the calorimeter is provided with a heating coil (in the form of a resistor). If a known current $I$ (amp) is passed for time $t$ (sec) through the heating coil. "Joule heating" will cause the temperature of the system to increase by (say) $\Delta T h$ (°C). The amount of energy supplied $Q$ (Joules) is,

$$Q = I V t \quad \text{--- (ii)}$$

where $V$ is the voltage drop across the heater resistance. Combining Equations (i) and (ii),

$$I V t = m C_p \Delta T + K \Delta T \quad \text{--- (iii)}$$

Using equation (iii), $C_p$ of a pure liquid of a solution may be determined (the other quantities being known experimentally).

(3) Determining partial molar enthalpies and molar enthalpies at infinite dilution

- $H_{1p} = H_m + x_2 \cdot \frac{dH_m}{dx_1}$ (iv)
- $H_{2p} = H_m - x_1 \cdot \frac{dH_m}{dx_1}$ (v)

- Put $x_2 = 1$ and determine the slope ($\frac{dH_m}{dx_1}$) at $x_1 = 0$ in (iv) to get $H_{1\infty}$
- Put $x_1 = 1$ and determine the slope ($\frac{dH_m}{dx_1}$) at $x_2 = 0$ in (v) to get $H_{2\infty}$

Suggestions to improve the experiment rig or calculation technique will be given extra credits.