INTEGRAL HEAT OF DISSOLUTION (calorimetric method)

1. PURPOSE OF THE WORK

Determination of the integral heat of dissolution of a solid.

2. THEORETICAL NOTIONS

The heat of dissolution (the thermal effect that accompanies the dissolution of a substance) depends on both the nature of the substance to be dissolved and the nature of the solvent, the temperature and the concentration of the solution obtained. According to the usual terminology, by ***integral heat of dissolution*** is meant the thermal effect that accompanies the dissolution of one mole of substance in a given amount of solvent. The ***differential (partial) heat of dissolution*** is the thermal effect that accompanies the dissolution of one mole of substance in an amount of solution so large that the change in concentration is practically zero. In the case of processes that occur at constant pressure or constant volume, the amount of heat exchanged with the environment is called the isobaric thermal effect ($Q_p = \Delta H$), respectively isochoric ($Q_v = \Delta U$).

Dissolving one mole of KCl in 400 moles of water, which is done with a consumption of 18438.2 J, can be formulated by the following thermochemical equation:

$$KCl + 400\ H_2O = KCl\ (aq\ 400) \qquad \Delta^{diz}H = 18438{,}2\ J \tag{1}$$

According to the law of heat exchange, the thermal effect of any process that takes place in the calorimeter is given by the relation

$$Q=(m_1c_1+m_2c_2+m_3c_3)\Delta\theta \tag{2}$$

where - Q - the thermal effect of the process performed in the calorimeter;

- m_1 - mass of the metal parts forming part of the calorimeter,
- m_2 - mass of calorimetric liquid
- m_3 - mass of the portions of the glass pieces immersed in the calorimetric liquid;
- c_1, c_2, c_3 - specific heats of the above materials
- $\Delta\theta$ - temperature variation.

The above equation can be written

$$Q = W \cdot \Delta\theta \tag{3}$$

where W is the water equivalent of the calorimeter or **calorimetric constant**.

To determine the integral heat of dissolution, the working steps are:

1. establishing the water equivalent of the calorimeter;

2. determination of the thermal effect of the dissolution by measuring the temperature variation of the calorimeter during the process.

The *water equivalent* of the calorimeter can be determined experimentally, either by performing in the calorimeter a chemical process whose thermal effect is known, or by passing through the calorimeter a known amount of electricity and observing the variation of the calorimeter temperature. The amount of heat required to heat the calorimeter with $\Delta\theta$ is, according to Joule's law,

$$Q = W \cdot \Delta\theta = U \cdot I \cdot t \quad (4)$$

from which the calorimetric constant is deduced

$$W = \frac{Q}{\Delta\theta} = \frac{U \cdot I \cdot t}{\Delta\theta} \quad (5)$$

in which: *U* - voltage, V

I - current intensity, A

t - time, s;

W results in J/degree and represents the amount of heat required to raise the calorimeter temperature by one degree.

Temperature measurement

After the calorimetric assembly has been prepared, start the stirrer and wait 3 minutes to reach the state of thermal equilibrium, which is recognized by a stationary temperature regime (the temperature remains constant for 4-5 minutes before starting the process). Note this initial value of the temperature with θ_i, after which the studied process can be started. It is observed that the temperature increases or decreases (as the process is exothermic or endothermic) at first faster and then more and more slowly, with the evolution of the process, because after a shorter time (for mixing two liquids) or more for a long time (to dissolve a solid), to remain constant again. Note this final temperature value with θ_f and check if it remains constant for another time, 4-5 minutes. Calculate the variation Δθ:

$$\Delta\theta = \theta_f - \theta_i \quad (6)$$

The duration of temperature observation can be divided as follows into three periods: ***the initial period*** - before the onset of the phenomenon studied (reading the initial temperature); ***the main period*** (in which the studied process takes place) - between the moments of reading the initial and final temperatures; ***the final period*** - after reading the final temperature. However, it may happen that the temperature does not remain constant in the initial and final periods, but a slight increase or decrease can be observed. In this case it is necessary to make certain corrections, as a result of which the temperature values are read from minute to minute during the three periods.

The temperature variation obtained by relation (6) is correct only in the ideal case. In reality, it also contains contributions due to secondary processes such as: evaporation of the liquid, friction of the liquid stirrer and the exchange of heat with the outside, which, no matter how low, must be taken into account. All these secondary contributions must be removed from the value of the measured temperature variation in order to obtain its correct value, usable in relation (5). For this, a corrected temperature variation, $\Delta\theta^*$, is calculated with the equation

$$\Delta\theta^* - \Delta\theta = \frac{1}{2}\left[\left(\frac{\Delta\theta}{\Delta t}\right)_i + \left(\frac{\Delta\theta}{\Delta t}\right)_f\right] \cdot t_p \qquad (7)$$

where $\Delta\theta$ - temperature variation between the first and last reading in the main period;

$\left(\frac{\Delta\theta}{\Delta t}\right)_i$ - temperature variation from the initial period relative to the duration of the same period;

$\left(\frac{\Delta\theta}{\Delta t}\right)_f$ - temperature variation in the final period relative to the duration of the same period;

t_p - the duration of the main period.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- calorimeter, digital direct current power supply with voltage and current display, stirrer, heater, thermometer, stopwatch, funnel, distilled water, salts to be studied.

3.2. PROCEDURE

The aim of the work is to determine the integral heat of dissolution at a temperature close to that of the chamber and at a final concentration of 1 mol salt to 200 mol water. For this purpose, the calorimeter constant is determined first and then the temperature variation caused by the dissolution of the salt.

The calorimeter used in this paper is of the type of adiabatic calorimeters with thermal insulation jacket. The calorimeter consists of a Dewar vessel fixed with an asbestos ring in a glass vessel, which in turn is insulated with expanded polystyrene on the outside. The asbestos ring has the role of preventing heat loss. A thermometer, a stirrer and a heater enter the Dewar vessel through the lid of the calorimeter. The stirrer is driven by a motor whose rotational speed can be adjusted with a rheostat. The calorimeter heater is connected to a direct current source. The current in the circuit and the voltage at the terminals of the heating element are measured.

Fill the calorimeter with 900 mL of water and place the lid of the calorimeter through which the agitator and the ends of the calorimeter heating element pass. Place the thermometer through the lid so that it measures the temperature in the calorimeter. Start the stirrer so that its rotational speed is moderate (if it is too low, it will not shake the mixture well enough and the salt to be added will not dissolve in a reasonable time; if it is very high, it may heat the water from the calorimeter). The stirring speed will be kept constant throughout the determinations. Start a stopwatch and read the temperature for 5 minutes every minute, noting the values in the results table. Note the constant temperature with θ_i (initial temperature).

At exactly 5 minutes, the DC power source starts. During heating, the temperature, current intensity and voltage at the terminals are read from minute to minute and are noted accordingly in the table. The heating is switched off after exactly 5 minutes by switching off the power supply. The temperature is observed for another 5 minutes after the heating is switched off. Note the constant final temperature with θ_f.

The values obtained for the temperature difference $\Delta\theta = \theta_f - \theta_i$ in the time interval *t*, the average of the values read for the intensity *I* and the voltage *U* are entered in relation (5) and the constant of the calorimeter is calculated, denoted by *W*.

Weigh a quantity of finely pulverized salt (the nature of which will be indicated by the teacher), necessary for the given amount of water corresponding to the ratio of 1 mol of salt to 200 moles of water.

Once the calorimeter constant has been determined, the thermal effect of the dissolution is measured. Without interrupting stirring, read the constant temperature before dissolution θ_i', similarly as above, reading the temperature every 30 seconds, for 8-10 minutes. At minute 3, add the salt to the calorimeter. Record the temperature after dissolution (~ 8-10 minutes at medium stirring), noting with θ_f' the constant final temperature. The temperature difference $\Delta\theta_{diz}$ is calculated with the relation: $\Delta\theta_{diz} = \theta_f' - \theta_i'$. The product *W* $\Delta\theta_{diz}$ = *q* is the thermal effect of dissolving the *m* grams of salt. For one mole of salt the thermal effect of the dissolution will be:

$$Q = \frac{M}{m} q \text{, J/mol} \tag{8}$$

where M is the molecular mass of the salt, m - the mass of the dissolved substance and q - the thermal effect of the dissolution.

4. EXPERIMENTAL DATA PROCESSING

4.1. The data are entered in tables of the form:

I. Determination of the calorimeter constant:

Time, min	0	1	2	3	4	**5**	6	7	8	9	**10**	11	12	13	14	15
Temperature, °C																
Voltage, V	-	-	-	-	-							-	-	-	-	-
Intensity, A	-	-	-	-	-							-	-	-	-	-

II. Determination of the thermal effect upon dissolution:

Time, min	0	0,5	1	1,5	2	2,5	**3**	3,5	4	4,5	5	5,5	6	6,5	7	7,5	8
Temperature, °C																	

4.2 From the experimental data the calorimeter constant is calculated

$$W = \frac{U \cdot I \cdot t}{\Delta\theta} \text{, J/grad}$$

4.3. The thermal effect of dissolution is calculated

$$q = W \cdot \Delta\theta_{diz} \text{, J} \qquad \text{total thermal effect}$$

$$Q = \frac{M}{m} q \text{, J/mol} \qquad \text{molar thermal effect}$$

The same relationships are used to calculate the calorimeter constant (notation W') and the thermal effect when dissolving one mole of salt (notation Q') using the corrected temperature variation denoted by $\Delta\theta^*$. The results are compared.

5. QUESTIONS

5.1. Give examples of endothermic and exothermic water dissolution processes.