HEAT OF DISSOLUTION OF A SOLID

(cooling curve method)

1. PURPOSE OF THE WORK

Determination of the dissolution heat of some solids (KNO_3 and naphthalene) by the method of cooling curves.

2. THEORETICAL NOTIONS

The dissolution process is generally accompanied by a heat exchange. For example, the dissolution of NH_4NO_3 in water takes place with heat absorption, and the dissolution of KOH in water gives off heat. If the process is performed at constant pressure, these thermal effects are the enthalpies of dissolution H, also called dissolution heat. The molar heat of dissolution depends on the concentration of the solution, reaching an extreme at saturation, where the thermal effect is $\Delta^d H^{\text{sat}}$.

In the case of an ideal eutectic mixture, the heat of dissolution to form a saturated solution is equal to the heat of melting of the solid. For this particular case the Schröder-Van Laar relation between the molar fraction of the solid and the temperature can be used:

$$\frac{d \ln X_{sat}}{dT} = \frac{\Delta^d H^{sat}}{RT^2} \qquad (1)$$

Integrating is obtained:

$$\ln X_{sat}(T) = -\frac{\Delta^d H^{sat}}{RT} + ct \qquad (2)$$

In the above relations X_{sat} is the solubility expressed by the molar fraction at saturation of the dissolved component, and T is the temperature at which the solid separates.

Representing graphically $\ln X_{sat} = f\left(\frac{1}{T}\right)$, you get a straight line with a slope $-\frac{\Delta^d H^{sat}}{R}$, which allows calculation of $\Delta^d H^{sat}$.

In the case of ideal solutions, the value of the molar heat for the formation of the saturated solution is the same for any solvent used and equal to the melting heat of the solid.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- thermostat with water bath, thermometer, magnetic stirrer, glass vials containing various

concentrations of the studied substances

3.2. PROCEDURE

There are 6 solutions with known molar fractions, placed in glass vials, in the shape of those shown in fig. 1. The vials are sealed to prevent vaporization of some of the components.

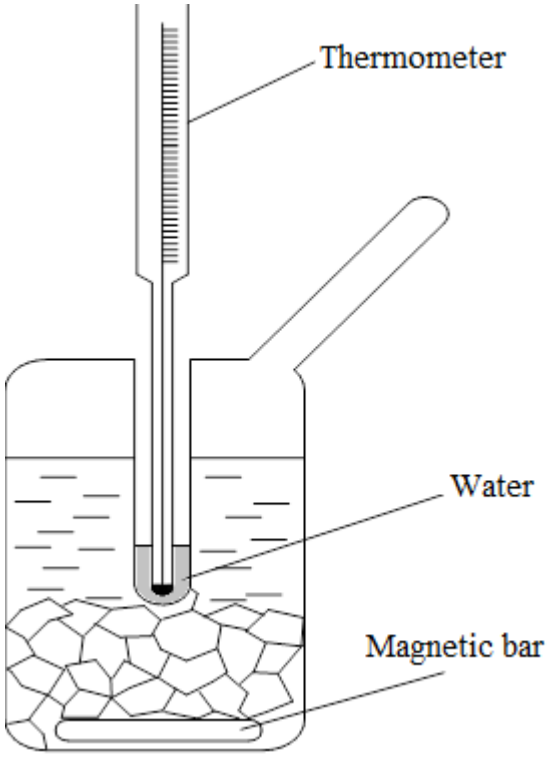

FIG. 1. Experimental vial

The samples to be studied are heated on a water bath and shake gently until the solid is completely dissolved. After all the solid in a vial has dissolved, the thermometer is carefully heated on the water bath and inserted into the inner tube of the vial while it is still in the bath. Carefully remove the vial from the hot bath to avoid scalding with the water remaining on the vial or its handle, empty the inner tube halfway so that the remaining water in the tube ensures thermal contact with the thermometer and a correct temperature reading. The vial is then clamped over the magnetic stirrer without touching it, and from this point on the temperature is read every 15 seconds until the reappearance of the crystals is observed and another 1.5-3 minutes after that. The procedure is repeated with each vial.

Note the values thus determined, observing the breaking point (change of slope) of the cooling curve $T = f(\text{time})$. By visual observation of the solution it is found that at the temperature corresponding to the change point of the slope of the cooling curve, the first crystals of the dissolved substance begin to deposit. This is the temperature at which the concentration of the solution has become the saturation concentration (i.e. the solubility of the solid at that temperature). Each vial is numbered and contains samples of known

compositions, listed in the table.

4. EXPERIMENTAL DATA PROCESSING

4.1. The experimental results are listed in the form tables:

Time, min	t, °C Vial 1	t, °C Vial 2	t, °C Vial 3	t, °C Vial 4	t, °C Vial 5	t, °C Vial 6
0						
0,25						
…						

(Obs. : The read temperatures can also be recorded as a list for each vial)

no. vial	**composition** X_{KNO_3} **or** $X_{naphtalene}$	**ln *X***	***t*, °C**	***T*, K**	**1/*T*, K^{-1}**	***m***	$\Delta^d H^{sat}$ **, J/mol**
H_2O + KNO_3							
1.	0,1021						
2.	0,1637						
3.	0,2000						
4.	0,2313						
toluene + naphthalene							
5.	0,4890						
6.	0,6020						
7.	1,0000						

4.2. Represent the temperatures read as a function of time (**cooling curve of a sample**), for all vials on the same graph;

4.3. The logarithm of the solubility as a function of the inverse of the absolute temperature is represented graphically, for the studied systems. Samples 1, 2, 3 and 4 contain KNO_3 and water, and samples 5 and 6 contain naphthalene and toluene. For the determination no. 7 (pure naphthalene sample), the value of the crystallization temperature is taken equal to the melting temperature of naphthalene given in the literature;

4.4. From the slopes of the two lines the dissolution enthalpies for the saturated solutions are calculated, with the relation:

$$\Delta^d H^{sat} = -R \cdot m \qquad (4)$$

where *m* is the slope of the regression line.

Data from the literature

$$T_{t,C_{10}H_8} = 80,26 \ ^\circ\text{C}$$

5. QUESTIONS

5.1. What happens to the temperature when the crystallization process begins? Explain. Give a practical example of where this phenomenon is used.

5.2. This experiment is the theoretical basis for at least one method of thermal analysis. Find a method of thermal analysis in the literature and describe it briefly.