

Determining enthalpy of dissolution

Theoretical background: P.W. Atkins: Physical Chemistry, 26.1–3.

Type of practice: Ondividual.

Purpose of practice: Introduction to calorimetry, how to determine thermodynamic data by calorimetry.

1 Introduction

Calorimetry is a method of measuring heat absorption or heat release that accompanies various physical and/or chemical processes. If there is no work in the process other than pressure–volume work, then in isobaric, reversible case the heat is equal to the enthalpy change of the system¹. The measuring equipment in calorimetry is called calorimeter. In nonisothermal calorimeters, heat can be calculated from the temperature change of the system under study (and/or the temperature change of its surrounding). The following must be taken into account for these calculations:

1. The amount of temperature change of the system depends on the heat capacity (sensitivity to heat) of the substances in the system under study. The definition of heat capacity at constant pressure is

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

that is, the heat capacity in numerical value is the heat that changes the temperature of the system by 1 K (or 1 °C). This value is generally not independent of the temperature, but can be considered constant over the temperature range used in the practice. That means, that the heat (Q) can be given simply as

$$Q = \Delta H = C_p \cdot \Delta T = C_p \cdot (T_{\text{final}} - T_{\text{initial}})$$

To evaluate the data measured with a calorimeter, it is essential to know the heat capacities of the substances in the system. In case of a one-component system, it is usual to refer the heat capacity to unit amount of substance ($C_{p,m}$). For multicomponent systems, we rather use the specific heat capacity (c_p) referring to unit mass. (Further on the subscript p will be omitted for the sake of simplicity, but all the equation will include heat capacities at constant pressure.)

2. The investigated process often does not take place instantaneously, which allows heat to be exchanged with the surrounding (environment), i.e., some of the heat to be determined disappears. This can be avoided either by using – usually expensive – thermal insulation materials and complex technical solutions, or by examining the pre- and post-life of the process. The latter method is illustrated in Fig. 1, where the curve on the left illustrates the measured temperature change of a process involving heat release and the curve on the right illustrates the temperature change of a process involving heat absorption. The process to be tested starts at time t_0 , but the system temperature is recorded long before it. The time between the start of temperature recording and the start of the process is called the pre-period. The start of the main period is t_0 and the main period includes the duration of the complete process studied. During the main period, the temperature change is determined by the heat of the process, but the heat exchange with the environment also begins. In the following post-period, the process, studied, has already taken place, here only the heat exchange with the surrounding determines the change in temperature. While a very sharp boundary can be drawn between the pre- and main periods at t_0 , the transition between the main and post-periods is continuous, as shown in Fig. 1. If the temperature change in the pre-period is approximately linear², extrapolating to t_0 , we can get

¹If the measurements are not made at a constant pressure but at constant volume, the change in internal energy can be determined as described.

²This temperature change can be traced back to causes other than the system under study (e.g., stirrer heating) and is called the calorimeter's shift.

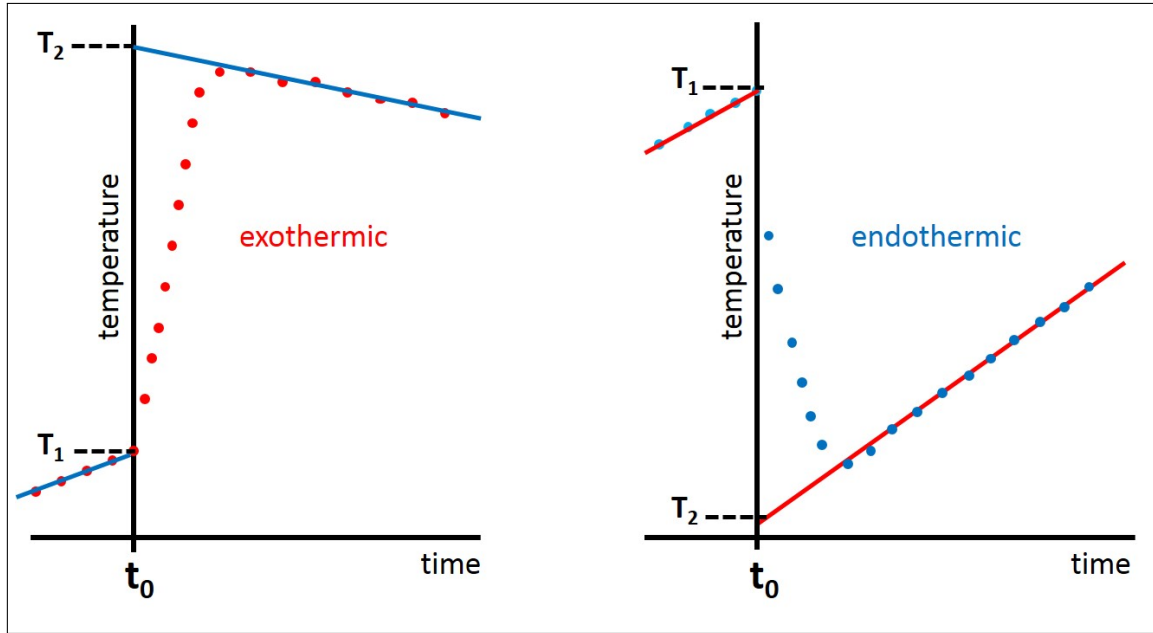


Figure 1: Calorimetric temperature – time curves and their evaluation.

the value T_1 , which is the temperature of the system at the moment when the process starts. If we extrapolate the post-period back to the time t_0 – also assuming linearity – we get the value T_2 . This is the temperature that would be measured if the process under study took place in an instant, i.e., there would be no time for heat exchange with the environment. The difference $T_2 - T_1$ is the total temperature change caused by the process if there was no heat exchange with the environment³.

3. The heat of the process changes not only the temperature of the system under study, but also the temperature of the apparatus, the calorimeter itself. The components of a calorimeter usually do not change, so the sum of the heat capacities of each part is constant, which can be given as the heat capacity of the calorimeter (C_{cal}). This is characteristic for a given device under similar measuring conditions, and actually it gives the heat required to change the temperature of the whole calorimeter by 1 K. The heat capacity of a calorimeter can be determined as follows.

To water of mass, m_a and temperature, $T_{1,a}$ in the calorimeter, add water of mass, m_b and temperature, T_b and measure the change in temperature as detailed in the previous section. If the temperature equalized only in water, the theoretical common temperature ($T_{2,theor}$) could be calculated on the basis of equality,

$$m_a \cdot (T_{2,theor} - T_{1,a}) = -m_b \cdot (T_{2,theor} - T_b) \quad (1)$$

In reality, however, $T_{2,com}$ is the common temperature, since some of the heat is absorbed by the components of the calorimeter, whose temperature changes from $T_{1,a}$ to $T_{2,com}$, as well. This can be considered by

$$c_w \cdot (m_a + m_b) \cdot (T_{2,theor} - T_{2,com}) = C_{cal} \cdot (T_{2,com} - T_{1,a}) \quad (2)$$

where c_w is the specific heat capacity of water at constant pressure. Expressing $T_{2,theor}$ from Eq. 1 and substituting into Eq. 2, we obtain

$$C_{cal} = c_w \cdot \left(m_b \cdot \frac{T_b - T_{2,com}}{T_{2,com} - T_{1,a}} - m_a \right) \quad (3)$$

By this equation, the heat capacity of the calorimeter can be calculated from the measurement data.

³Further on, the values of T_1 and T_2 for the different processes are indicated by a letter in the subscript

1.1 Determining the enthalpy of dissolution of solids

The enthalpy of dissolution (heat of dissolution) is the heat accompanying the complete dissolution of 1 mol substance. The dissolution of a solid can be separated to the following thermal processes:

- The temperature of the compound to be dissolved with a mass of m_{comp} varies from the room temperature, T_r to T_1 .
- During dissolution, the temperature of the water of mass m_w , the solute of mass m_{comp} and the parts of the calorimeter change from T_1 to T_2 .

If the heat, associated with dissolution is denoted by Q ,

$$Q = c_{\text{comp}} \cdot m_{\text{comp}} \cdot (T_1 - T_r) + (c_{\text{sol}} \cdot (m_w + m_{\text{comp}}) + C_{\text{cal}}) \cdot (T_2 - T_1) = -\Delta H_{\text{dissol}} \cdot n_{\text{comp}}, \quad (4)$$

where c_{comp} and c_{sol} is the specific heat capacity of the solid compound and the solution, n_{comp} is the amount of substance of the compound dissolved and ΔH_{sol} is the molar dissolution enthalpy of the compound in water.

1.2 Determining the heat capacities

It can be seen from the above that the heat of dissolution can be easily determined by measuring the change in temperature if the heat capacities are known and can be considered constant in the temperature range of the measurement. These values can be found in various tables. If such tables are not available, you can estimate the required values as follows:

- The specific heat capacity of water at the practice can be taken as $c_w = 4.183 \text{ J/(g K)}$.
- In dilute or medium-concentrated solutions, the value of the specific heat capacity can be estimated with an accuracy of about 1 % based on the Dimoplon equation:

$$c_{\text{sol}} = w_w \cdot c_w + w_{\text{comp}} \cdot c_{\text{comp}}, \quad (5)$$

where w_w is the mass fraction of water, and w_{comp} is the mass fraction of dissolved compound.

- The simplest way to estimate the molar heat capacity of solid compounds is by the Kopp rule, which states that the molar heat capacity of a solid compound can be approximated by the sum of the products of the molar heat capacities and stoichiometric coefficients of its elements (not the atoms but the elements!).⁴

$$C_{\text{comp}} = \sum_{i=1}^n \nu_i \cdot C_{m,i}$$

For example, for solid Na_2CO_3 :

$$C_m(\text{Na}_2\text{CO}_3) = 2 \cdot C_m(\text{Na}) + C_m(\text{C}) + \frac{3}{2} \cdot C_m(\text{O}_2),$$

where the corresponding data for the elements can be found in Table 1. The molar heat capacities that can be calculated in this way must be converted to specific heat capacities if we want to use them in the Eqs. 3 – 5. The relative atomic masses required for the calculation can be found in the periodic table in the Appendix.

⁴This rule does not apply to some compounds, but it is appropriate for solids that are tested in practice.

Table 1: Average molar heat capacity of some elements in the range of 283 – 311 K given in J/(mol K).

element	$C_{p,m}$	element	$C_{p,m}$	element	$C_{p,m}$	element	$C_{p,m}$	element	$C_{p,m}$
Al	24.1	B	11.9	Br ₂	37.7	C	9.7	Ca	26.4
Cu	24.6	H ₂	28.7	I ₂	37.7	K	28.8	Mg	24.4
N ₂	28.4	Na	27.6	O ₂	26.0	P	23.2	S	23.8
								Zn	25.3

2 Experimental

In the practice, the task is to determine the enthalpy of dissolution of a solid electrolyte by calorimetry. The "calorimeter" is a beaker with a stirring bar and a thermometer. At the beginning of the practice, the instructor selects the electrolyte to be tested and the temperature change to be planned between 4–9 °C. Unless the instructor says otherwise, the salt to be tested is ammonium nitrate and the planned temperature change is 5 °C. First, determine experimentally the mass of the salt to be dissolved in water so that the temperature change during dissolution is approximately equal to the planned. To do this, weigh ~ 20 g of water into a clean, dry, 50 cm³ beaker, insert a magnetic stirring bar and place the beaker on a magnetic stirrer. A thin sheet of polystyrene can be placed between the stirrer and the beaker so that the stirrer does not heat the system from below. The speed and position of the rotating stirring rod are adjusted so that the rod does not bounce, rotates stably and there is space for the thermometer. When placing the thermometer, make sure that the rotating stirring bar does not collide with the thermometer. Read the initial temperature. Add ~ 0.5 g of salt to the water suddenly, and observe the maximum or minimum temperature formed during dissolution. This point is sure to occur before complete dissolution, it is not worth measuring any further.

Knowing the temperature change obtained, you can calculate the mass of salt that is needed to be dissolved in ~50 g water for calorimetric measurements in order to get the planned temperature change. If the temperature in the preliminary experiment did not change so much that the required mass of the salt could be estimated to at least 20 %, repeat the experiment with twice the amount of salt, if this did not work, four times as much, and so on.

This is followed by the experiments required to determine the enthalpy of dissolution. This is done similarly to the preliminary experiment. Weigh into a clean, dry, 100 cm³ beaker, about 50 g water, with an accuracy of 0.01 g (m_w). Then weigh the mass of a clean, dry beaker of 25 cm³ and weigh in the calculated mass of solid. If the solid is not hygroscopic, the substance can be measured on a piece of paper (paper boat), but weigh also its mass before weighing the solid. Insert the magnetic stirring bar into the beaker containing the water, place the beaker on the stirrer and insert the thermometer as above. Then read the water temperature every half minute for 5 minutes with a rotating stirrer. This will be the pre-period. The solid is then poured into the water, and put aside the 25 cm³ beaker, or paper boat. Pouring the solid into water is t_0 time. Then, as often as you can, read the temperature and the corresponding time. This is continued until the rapid temperature change slows down or reverses, that was the main period⁵. In the post-period, the temperature is recorded every half a minute for about 10 minutes. After completion of the measurement, the put-aside beaker (or paper) is reweighed to calculate the exact mass of material actually dissolved (m_{comp}). The measurement is then repeated using the same 100 cm³ beaker, cleaned and dried before re-measuring. *The beaker can be dried by rinsing with a small amounts of technical acetone.*

Next, determine the heat capacity of the calorimeter in the same beaker of 100 cm³. This will be more accurate if you provide the most similar conditions to your previous measurements. This can be achieved by choosing the initial temperature and the masses of water m_a and m_b defined in Eq. 1 as follows:

- If the temperature decreased during the dissolution of the solid, make water of $T_b \sim 0$ °C with a mixture

⁵The time of the main period is highly dependent on the rate of dissolution of the salt, in the case of rapid dissolution we can only read a few points.

of water and ice, and take the water of mass m_b to be added. If the dissolution of the solid produced heat, warm water of $T_b \sim 50^\circ \text{C}$ to be added.

- The value of $T_{1,a}$ is approximated by the average of the values of T_1 from the previous measurements.
- The value of $T_{2,com}$ is approximated by the measured temperature that differs most from the value of T_1 in the previous measurements.
- The total mass of water used in the measurement should be approximately equal to the total mass of the solution tested in the previous experiments: $m_a + m_b = m_w + m_{comp}$. Using this relation, Eq. 1, and the estimated temperature values, the masses m_a és m_b to be used can be calculated.

After the result of the calculation has been checked by the instructor, the measurements are performed in the same way as before, with three differences:

- Weigh the mass of room temperature water, m_a , the beaker and the stirring bar together (calorimeter) before starting the measurement.
- In order to start the main period as quickly as possible, the calculated mass of water (m_b) is added to the water in the beaker from a graduated cylinder. The exact mass of the added water m_b is determined later from mass measurements. Cool or warm the water in the graduated cylinder in a $300 - 600 \text{ cm}^3$ beaker. A second thermometer is placed in the cooled or warmed water (preferably in the measuring cylinder) and the exact temperature is read just before the water is poured out the cylinder. Mixing of waters with different temperatures takes place very quickly, so it may be that only one or two points can be read in the main period.
- After the post-period, the mass of the beaker together with the water and the stirring rod is weighed again in order to calculate the exact value of m_b .

To determine the heat capacity of the calorimeter, two parallel measurements must be made, again using the same beaker of 100 cm^3 , cleaned and dried before repeating the measurement.

3 Evaluation

- The measured $T - t$ data are arranged in tables, indicating the time of the beginning of the main period.
- Plot all four series of measurements by showing the moment of t_0 in the figure. The axes should be chosen so that the values of T_1 and T_2 (or $T_{2,com}$) could be determined by simple graphical extrapolation (or straight line fitting, if you can use a computer program). Determine the value of these temperatures in all four measurements. It is not necessary to specify the statistical parameters of the fitted lines.
- From the last two measurements, calculate the values of C_{cal} using Eq. 3 and use their average for further calculations.
- Using the Kopp rule and the molar masses, calculate the molar and specific heat capacity of the tested compound ($C_{m,comp}$ and c_{comp}), then using the Dimoplon equation given by Eq. 5, calculate the specific heat capacity of the solution (c_{sol}). If the compound, tested, contains water of crystallization, then $C_{m,comp}$, c_{comp} and c_{sol} values shall be calculated for the anhydrous salt, the measured value of m_{comp} shall be reduced by the mass of the water of crystallization, while the value of m_w shall be increased by the same mass.
- From the first two measurements, calculate the enthalpy of dissolution of the compound using Eq. 4, and give their average as the final result. The measured data and the results of the calculations are summarized according to Table 2–3.
- Find literature data (indicating the source) for the value of the dissolution enthalpy and compare that with the measured data. Try to explain any significant differences.

Table 2: Summary of the measured data.

	m_w (g)	m_{comp} (g)	n_{comp} (mol)	T_1 (°C)	T_2 (°C)	T_r (°C)	$C_{m,\text{comp}}$ (J/mol/K)	c_{comp} (J/g/K)	c_{sol} (J/g/K)	ΔH_{dissol} (kJ/mol)
1. meas										
2. meas										
	m_a (g)	m_b (g)	T_{1a} (°C)	T_b (°C)	$T_{2,\text{com}}$ (°C)	C_{cal} (J/K)	$C_{\text{cal,average}}$ (J/K)			
3. meas										
4. meas										

Notes:

- The crystals of the solid may have clumped together. In this case, 5 – 10 g must be pulverized with the available mortar and pestle before starting the experiments. However, this should not be done if the material consists of hygroscopic or factory compacted pellets (e.g., NaOH, KOH)!
- The dissolution of some salts (especially factory compacted pellets) can be very slow if the rotation of the stirring bar is too slow. Stirring should be rapid enough to form a small/shallow cone on the surface of the solution.
- In the practice several notations is introduced. These should be understood before laboratory work and should not be confused. Otherwise, there is a high probability that you will not measure something that would be needed for the evaluation.
- Because each of the equation used for the calculations contains temperature differences, the temperature values in either °C or K can be used.

Questions

1. What is calorimetry and calorimeter?
2. Define heat capacity? What is the difference between heat capacities at constant pressure and at constant volume?
3. What is molar and what is specific heat capacity? How do we mark these?
4. Explain in 3–4 sentences what is the pre, main and post period in a measurement?
5. Define the heat capacity of the calorimeter! Why is it important to determine this value?
6. What is the enthalpy of dissolution?
7. What is the Dimoplon equation and what can it be used for?
8. What is the Kopp rule?
9. How do you determine the mass of solid to be dissolved during the exercise?
10. How do you ensure similar measurement conditions when determining the heat capacity of a calorimeter and measuring enthalpy of dissolution?
11. Dissolving 0.5 g of solid NaOH in 20.3 g water, the observed temperature change was 6.1 °C. How many grams of NaOH need to be dissolved in 49.3 g water if we want a temperature change of 5.3 °C?
12. Water of X g, 25,0 °C and Y g, 50,0 °C to be mixed so that to give a total of 56.71 g, 31.2 °C of water. What are the values of X and Y if there is no heat loss?
13. Dissolve 4.17 g of KNO₃ in 50.73 g of water. What will be the specific heat capacity of the resulted solution based on the Dimoplon equation? $c_w = 4.183 \text{ J g}^{-1} \text{ K}^{-1}$, $C_{m, \text{KNO}_3} = 82.0 \text{ J mol}^{-1} \text{ K}^{-1}$ and $M_{r, \text{KNO}_3} = 101.10$.
14. What is the molar heat capacity of Al₂(SO₄)₃ according to Kopp rule? The molar heat capacity of elements in J mol⁻¹ K⁻¹ units: Al: 24.1; S: 23.8 és O₂: 26.0.