# 05. Enthalpy of hydration of sodium acetate

## Important concepts

The law of energy conservation, extensive and intensive quantities, thermodynamic state functions, heat, work, internal energy, enthalpy, constant volume heat capacity, constant pressure heat capacity, specific heat capacity, molar heat capacity, reaction enthalpy, Hess's law, non-isotherm calorimeter, adiabatic calorimeter, constant pressure calorimeter, Dewar-flask, heat leakage of calorimeter, heat capacity of heat absorbing parts, Joule heat, reaction extent.

## Objective

The determination of the reaction enthalpy of this process:

$$CH_3COONa(s) + 3\,H_2O \longrightarrow CH_3COONa \cdot 3\,H_2O\,(s) \qquad \text{R0}$$

We will determine this value by measuring the enthalpies of solution for anhydrous sodium acetate and for sodium acetate trihydrate. Application of Hess's Law will give us the $\Delta_r H$ for the hydration reaction.

$$CH_3COONa(s) \xrightarrow{excess\ H_2O} CH_3COO^-(aq) + Na^+(aq) \qquad \text{R1}$$

$$CH_3COONa \cdot 3\,H_2O\,(s) \xrightarrow{excess\ H_2O} CH_3COO^-(aq) + Na^+(aq) + 3\,H_2O \qquad \text{R2}$$

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The solution of the anhydrous salt, process R1 produces $\Delta_r H_1$ solution for the anhydrous salt, and the solution of the trihydrate, process R2 involves $\Delta_r H_2$ solution for the sodium acetate trihydrate.

Application of Hess's Law means the subtraction of processes R1 – R2,

$$CH_3COONa(s) - CH_3COONa \cdot 3\,H_2O\,(s) = -3\,H_2O$$

rearranging we get

$$CH_3COONa(s) + 3\,H_2O \longrightarrow CH_3COONa \cdot 3\,H_2O\,(s)$$

which process is identical to R0, the process for which enthalpy is to determine. Therefore the measured enthalpy difference for R1 and R2 is given as

$$\Delta_r H = \Delta_r H_1 - \Delta_r H_2 \qquad 1.$$

## Calorimetry

In calorimetric experiments generally the temperature change accompanying a chemical reaction or phase transfer is measured. For calculating heat involved in these processes, in a separate experiment, the heat capacity is determined. In a constant volume calorimetric experiment internal energy is determined. In a constant pressure calorimetric experiment enthalpy is determined.

Enthalpy is a function of temperature, pressure and amount of material: $H(T,p,n)$**.** As we treat an isolated system, we omit the dependence on $n$ the partial derivatives are given

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

At constant pressure, d$p$ = 0

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT \qquad 2.$$

where $\left(\frac{\partial H}{\partial T}\right)_p = C_p$ is the heat capacity at constant pressure. The enthalpy change for processes , e.g. heat of combustion, heat of boiling or fusion etc., can be determined by taking the integral of function in Equation 2. between states 1 and 2,

$$\int_1^2 \mathrm{d}H = C_p \int_1^2 dT$$

which is easy to integrate, if $C_\mathrm{p}$ is not a function of $T$ in the interval $T_1$ and $T_2$.

$$H_2 - H_1 = \Delta H = C_p \Delta T \qquad 3.$$

In liquid phase and at small temperature changes ($\Delta T$) the work $p\Delta V$ can be neglected, therefore

$$q = \Delta H \qquad 4.$$

The heat capacity can be given

$$C_\mathrm{p} = \sum c_i m_i$$

as the sum of products of specific heat, $c$ (J kg$^{-1}$ K$^{-1}$) and mass, $m$ (kg) of the surrounding components of reacting system. In calorimetry, it is customary to separate the heat capacity of calorimeter liquid (e.g. water) from the heat capacity of other heat absorbing components

$$C_\mathrm{p} = c_\mathrm{w} m_\mathrm{w} + \sum c_\mathrm{j} m_\mathrm{j} \qquad 5.$$

where $c_\mathrm{w}$ = 4.185 J g$^{-1}$K$^{-1}$, the specific heat of water.

Reaction mixture is often a dilute aqueous solution, so the specific heat of the solution can be taken equal to that of water.

When heat that is released by the chemical reaction, then temperature of the solution in which the reaction takes place and heat absorbing parts of calorimeter will increase. In this sense, we regard the amount of materials of chemical reaction as *system* and calorimeter liquid together with the heat absorbing parts of calorimeter as surroundings. Assuming that no heat is lost, then the heat released by the chemical reaction must be transferred to calorimeter liquid together with the heat absorbing parts of calorimeter, and we can write

$$q_\mathrm{surr} + \Delta H = 0 \quad \text{and} \quad q_\mathrm{surr} = -\Delta H \qquad 6.$$

If $\Sigma H$(products) - $\Sigma H$(reactants) < 0 the reaction is *exothermic*, so the calorimeter warms up.

Now we change extensive variable $\Delta H$ (unit: J) to an intensive one $\Delta_\mathrm{r}H$, the reaction enthalpy (unit: J mol$^{-1}$) in order to give this state function independent of stoichiometry and the amount of material of reactants and products.

The intensive variable $\Delta_\mathrm{r}H$ is defined for a chemical reaction as

$$\Delta_r H = \frac{\Delta H}{\Delta \xi} = \sum \nu_i H_i \qquad 7.$$

where $\nu_i$ is the stoichiometric number, $\nu_i < 0$ for reactants and , $\nu_i > 0$ for products. The reaction extent, $\Delta\xi$ for the i$^{th}$ component.

$$\Delta\xi = \frac{n_i - n_{0,i}}{\nu_i}$$

The reaction extent is independent of reacting components and given in moles. In our case the solution process goes to a completion, therefore $\Delta\xi = n_{salt}$.

$$\Delta_r H = \frac{\Delta H}{n_{\text{salt}}} \qquad \text{7a.}$$

**Constant pressure calorimeter**

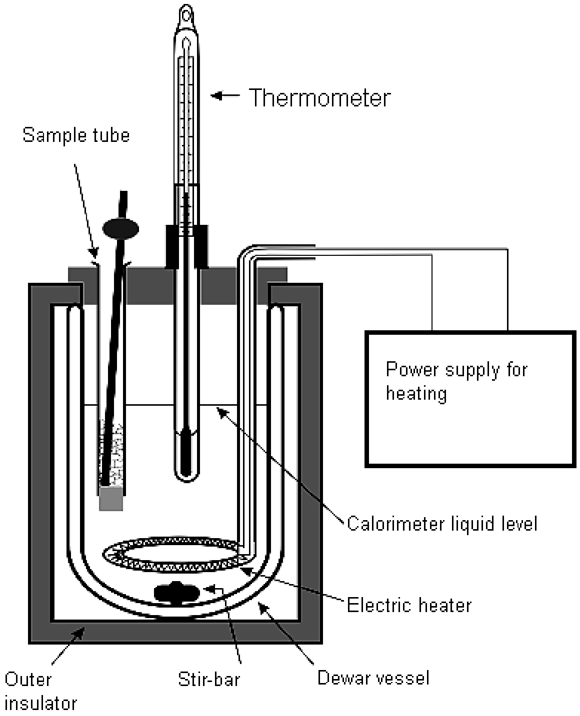

Figure 1. A constant pressure (open) calorimeter with adiathermal walls, which prevent heat leaking. This is used in experiments.

A *constant volume* calorimeter (bomb calorimeter) is closed when it operates, therefore it is applicable to determine internal energy of chemical reactions. The internal pressure of bomb calorimeter in most of the experiments (combustion reactions) increases, but there is no pV work done by the system. The temperature of reacting system is monitored.

A *constant pressure* (open) calorimeter is a device in which different chemical reactions or phase transformation processes etc. mostly in liquid phase can be carried out. The reaction heat of these processes cause temperature changes, which can be measured by thermometer.

A precisely measurable amount of heat can be generated by electric heater, this heat causes also a temperature difference. The heat capacity of calorimeter can be calculated from that temperature difference. From the thermally insulated vessel only a very small amount of heat can leak, therefore the temperature difference measured is proportional to the heat capacity of calorimeter. The small heat loss can be corrected by graphical method from the temperature vs. time function (see Figure 2.) taken during the heat transfer process. The temperature distribution in the calorimeter liquid should be even, which is maintained by mixing it with a stir-bar.

*Determination of the heat capacity of calorimeter, process A (calibration)*
In the sense of thermodynamics, *system* consists of components either in R1 or R2 reaction.
The components of *surroundings* (heat absorbing parts) are:

calorimeter liquid (400 ml or 400 g of water),
the immersing body of the heater,
the immersing body of the thermometer,
the internal wall of Dewar vessel, etc.

The enthalpy change produced or absorbed by the system transfers heat, $q_{\text{surr}}$, which causes an increase or decrease in temperature of surroundings. It is measured as temperature difference. From Eqs. 3. and 6. we have

$$q_{\text{surr}} = C_p \cdot \Delta T_1 = -\Delta H \qquad 8.$$

where $\Delta T$ is the observed temperature difference. The temperature difference $\Delta T_1$

$$\Delta T_1 = T_2 - T_1$$

is strictly the difference between the final and initial temperature taken from $T$ vs. $t$ graph (see Figure 2.). This temperature difference will decide the sign of reaction enthalpy.
The heat capacity of heat absorbing parts is determined by an electric heater. The heater having a resistance, $R$, is operated at constant voltage, $U$, and it is switched on a measured time interval. The heat produced by the electric heater is equal to work done by the current flowing through the resistance for time, $t$.

$$q_{\text{surr}} = C_p \cdot \Delta T_1 = \frac{U^2}{R} t \qquad 9.$$

When $U$ is given in Volts, $R$ in Ohms and $t$ in seconds the unit of $C_p$ is J $K^{-1}$ .

*Determination of the heat of reaction, process B*
Carrying out the solution process with anhydrous sodium acetate first, we observe a temperature difference:

$$\Delta T_2 = T_4 - T_3$$

The sign of this difference is positive for exothermic process, but it is negative when endothermic process takes place in the calorimeter.

The heating and solution processes are carried out in the same run, therefore, we suppose $C_p$ remains the same. The reaction enthalpy for solution of anhydrous sodium acetate is given,

$$\Delta_r H_1 = \frac{C_p}{n_{\text{salt}}} \cdot \Delta T_2 \qquad 10a.$$

In the second experiment we determine the actual value of $C_p$ (see also procedure part) and the heat caused by the solution of sodium acetate trihydrate. For that we have

$$\Delta_r H_2 = \frac{C_p}{n_{\text{salt}}} \cdot \Delta T_2 \qquad 10b.$$

From Equations 1., 10a. and 10b. we are able to calculate the enthalpy of hydration of sodium acetate.

For being an intensive variable, the value of $\Delta_r H$ is independent of the final salt concentration, but the solution process gives different reaction enthalpy changes at different amount of salt added. (You dissolve the last portions of solid salt in a salt solution and not in pure water.) In order to avoid these problems we prepare almost equimolar solutions of anhydrous and hydrated sodium acetate respectively.

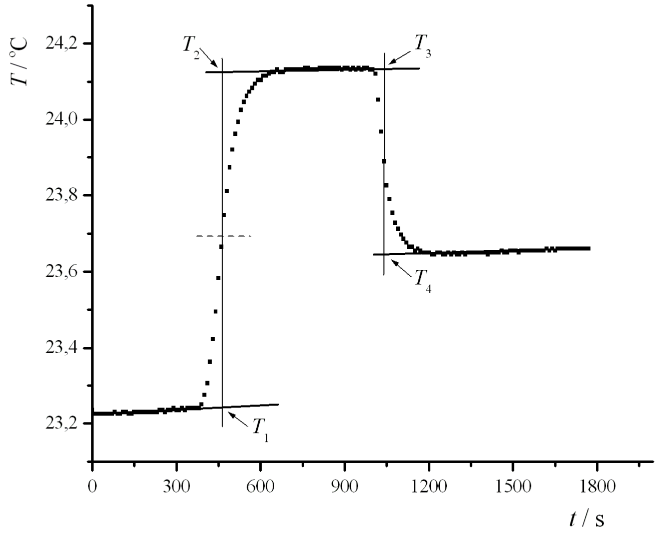

Figure 2. Tracking the temperature of calorimeter in time.

## Procedure

Students will carry out two experiments, one with anhydrous sodium acetate and another with sodium acetate trihydrate. The procedure part for both experiments are very similar.
One experiment is about a continuous temperature sampling by 20 s time intervals during the course of process A and B. The data are to be written in the datasheet you get from instructor.

1. Dry the sample tube and fit a cork to the bottom of the tube. Hold the tube with closed end downward, and immerse it into molten paraffin. Therefore the tube is isolated from getting calorimeter liquid into it.
2. Using graduated cylinder, measure out some 400 ml of distilled water and pour it into the dry Dewar vessel. Use the same graduated cylinder for both experiment. Place into the Dewar vessel: the electric heater, the stirbar and the thermometer. Start mixing the liquid. Do not interrupt mixing during the experiment. From time to time take a glance on the stirrer.

Note:
**Always hold the heater in vertical position, do not turn it upside down. Therefore you avoid oil leaking from it.**

3.a In the first experiment place sample tube on the balance and tare the balance, than measure into the sample tube 4 – 5 g of **anhydrous sodium acetate** by four digit precision.

Datum to be noted: mass of anhydrous sodium acetate

3.b In the second experiment place sample tube on the balance and tare the balance, than measure into sample tube from **sodium acetate trihydrate** exactly 1.659 times the mass of anhydrous sodium acetate by four digit precision.

Datum to be noted: mass of sodium acetate trihydrate

Molar masses:
anhydrous sodium acetate, 82.03 g mol$^{-1}$
sodium acetate trihydrate, 136,09 g mol$^{-1}$
Molar ratio: 136.09 / 82.03 = 1.659

4. Place the sample tube in the calorimeter and wait 5 minutes for establishing thermal equilibrium.

5. Start taking temperature reading in time. (Start filling the pre-printed table with data.) The frequency of reading for the whole experiment (stage 1 - stage 5) is 20 seconds.

You read the mercury thermometer for four significant digits, e.g. 22.16 °C. The last decimal (22.1**6**) should be estimated.

5/1. Stage 1 (observing temperature equilibrium) will last 3 – 5 minutes. When you have about 5 identical temperature data finish stage 1 and turn to stage 2.

5/2 In Stage 2 (heating stage) the heater should be ON for 60 seconds. (When more than 60 s is applied for heating, than that value of time is used for heat calculations.) You will observe an increase in temperature. Parameters like output voltage of power supply, electric resistance of your heater and the precise time interval of heating should be noted for calculations.

Data to be noted: output voltage, electric resistance and time interval of heating.

5/3 In stage 3 (observing temperature equilibrium) you continue reading data until about 6 identical temperature data are collected (3 – 5 minutes). From this data section, you will identify the final temperature of heating stage, and at the same time this temperature will be the starting temperature of solution process.

5/4 At the beginning of stage 4 (solution process) you push cork by a glass rod and help dissolving all the salt by mixing vigorously the solution with glass rod for half a minute.

5/5 In stage 5 (observing temperature equilibrium) you continue to note readings until solution process reaches its temperature equilibrium (4 – 5 minutes).

6. Reset the starting circumstances of experiment and repeat procedure 1. → 5. with sodium acetate trihydrate.

**Steps of calculation**

1. Plot two $T$ vs. $t$ functions like Figure 2. on mm-paper. One for anhydrous sodium acetate and another one for sodium acetate trihydrate. From the three approximately horizontal sections of the graph determine $T_1$, $T_2$, $T_3$, $T_4$. In most of the cases $T_2$, and $T_3$ will be identical. Calculate the adequate $\Delta T_1$ and $\Delta T_2$ values.
2. Calculate electric work and $C_\mathrm{p}$ separately for the first and second run. Use Equation 9.
3. Test the goodness of the first part of your experiment. Calculate product $c_\mathrm{w} m_\mathrm{w}$. Use Equation 5. for the test. If inequality

$$C_\mathrm{p} - c_\mathrm{w} m_\mathrm{w} \le 0$$

does exist (gives negative value or zero) for the one or both experiments consult your instructor what to do. If not calculate the average of the two calculated $C_p$ value. For the following calculations use this average.

4. Calculate $C_{p,M}$ from $C_p$ average, taking into account the formula: $C_{p,M} = C_p/n_{salt}$.

5. Determine the reaction enthalpies $\Delta_r H_1$ and $\Delta_r H_2$.by using Eqs. 10a. and 10b.

Finally, calculate $\Delta_r H$ in J mol$^{-1}$ or kJ mol$^{-1}$ units from Eq. 1. Be careful in deciding the sign of component reaction enthalpies (see Eq. 8.).

**Sample calculation (data Tóth, Jandrasits, 2007)**

$R = 23.9\ \Omega$, $U = 24.5$ V, $t$(heating) = 80 s

**Anhydrous sodium acetate**

mass: 4.203 g, molar mass: 82.03 g/mol, n = 4,203/82.03 = 0.0512 mol.

$$Q_{electric} = \frac{U^2 t}{R} = \frac{24.5^2 \cdot 80}{23.9} = 2009.2\,\mathrm{J}\text{, is the Joule heat.}$$

$$Q_{electric} = q = C_p \Delta T_1 \Rightarrow C_p = \frac{q}{\Delta T_1} = \frac{2009.2}{0.95} = 2114.95\ \mathrm{J/K}$$

Test:

Heat absorbing parts: $q_{hap} = C_p - c_w m_w = 2114.95 - 4.185 \cdot 400 = 2114.95 - 1674 = 440.95$ J/K

**Sodium acetate trihydrate**

mass: 6.972 g, molar mass: 136.09 g/mol, n = 6.972/136.09 = 0.0512 mol.

$$Q_{electric} = \frac{U^2 t}{R} = \frac{24.5^2 \cdot 60}{23.9} = 1506.9\,\mathrm{J}\text{, is the Joule heat.}$$

$$Q_{electric} = q = C_p \Delta T_1 \Rightarrow C_p = \frac{q}{\Delta T_1} = \frac{1506.9}{0.82} = 1837.7\ \mathrm{J/K}$$

Test:

Heat absorbing parts: $q_{hap} = C_p - c_w m_w = 1837.7 - 4.185 \cdot 400 = 1837.7 - 1674 = 163.7$ J/K

**$C_p$ average**

$$\bar{C}_p = \frac{2114.95 + 1837.7}{2} = 1976.3\ \mathrm{J/K}$$

**Reaction enthalpy of anhydrous sodium acetate, $\Delta_r H_1$**

$q_{surr}/n_{salt} = -\Delta_r H_1$

$$\frac{q_{surr}}{n_{salt}} = \frac{1976.3 \cdot 0.49}{0.0512} = 18914\ \mathrm{J/mol}$$

$\Delta_r H_1 = -18.914$ kJ/mol

**Reaction enthalpy of sodium acetate trihydrate, $\Delta_r H_2$**

$$\frac{q_{\mathrm{surr}}}{n_{\mathrm{salt}}} = \frac{1976.3 \cdot (-0.67)}{0.0512} = -25862 \text{ J/mol}$$

$$\Delta_r H_2 = 25.862 \text{ kJ/mol}$$

**$\Delta_r H$ for the hydration reaction**

$$\Delta_r H = \Delta_r H_1 - \Delta_r H_2 = -18.914 - 25.862 = -44.776 \text{ kJ/mol}$$

## Sample questions and answers for the minimum level tests (MLT).

MLT is devoted for practicing and preparing to labs at home, and its topical list covers the problems we discuss at the beginning of the lab.

### MLT Q and A

Q0 What are the extensive and intensive properties?
A0 An intensive property (also called a bulk property), of a system that does *not* depend on the system size or the amount of material in the system.
By contrast, an **extensive property** of a system *does* depend on the system size or the amount of material in the system.

Q1. How would you apply Hess's law to hydration reaction of sodium acetate?
A1. The reaction enthalpy of hydration reaction,

$CH_3COONa(s) + 3\ H_2O \rightarrow CH_3COONa \cdot 3\ H_2O\ (s)$

cannot be determined by calorimetry. However, the enthalpy of two component solution processes can be measured in a calorimeter. Taking the difference of these two solution processes

$$CH_3COONa(s) \xrightarrow{excess\ H_2O} CH_3COO^-(aq) + Na^+(aq) \qquad \Delta_r H_1$$

$$CH_3COONa \cdot 3\ H_2O\ (s) \xrightarrow{excess\ H_2O} CH_3COO^-(aq) + Na^+(aq) + 3\ H_2O \qquad \Delta_r H_2$$

we obtain the hydration process itself,

$$CH_3COONa(s) - CH_3COONa \cdot 3\ H_2O\ (s) \rightarrow -\ 3\ H_2O$$

which rearranges

$$CH_3COONa(s) + 3\ H_2O \rightarrow CH_3COONa \cdot 3\ H_2O\ (s) \qquad \Delta_r H_3$$

and for reaction enthalpies we get: $\Delta_r H_3 = \Delta_r H_1 - \Delta_r H_2$. We used up the state function property of enthalpy.
Q2. Why we use stirbar and double walled insulator tube in calorimeter?
A2. To maintain the condition of even distribution of temperature and concentration throghout the vessel. Insulator walls prevent heat transfer to laboratory.
Q3. What is the difference between enthalpy and reaction enthalpy?
A3. Enthalpy is a state function but an extensive variable, while reaction enthalpy is also a state function but an intensive variable which is independent of the extension of the system.

Q4. Why we use electric heater for the determination of heat capacity of calorimeter.
A4. We produce a certain heat which is absorbed by the calorimeter liquid. The magnitude of heat can precisely adjusted by changing parameters *R*, *t* or *U*, phrased in equation

$$q_{\mathrm{surr}} = C_p \cdot \Delta T_1 = \frac{U^2}{R} t \, .$$

Q5. What is the reason for determining heat capacity of heat absorbing parts?
A5. All the parts of the calorimeter (glass ending of thermometer, internal wall of Dewar-flask etc.) except the calorimeter liquid belong to this group, and each of the different materials has its own specific heat capacity. They will absorb an amount of heat when heat is evolved in the calorimeter. Without taking heat absorbing parts into account, the calculated enthalpy would contain subjective error.

Q6. How long an electric heater is to be operated, when the temperature of calorimeter should be increased by 2.2 °C? The heater's resistance *R*= 24 Ω, its operating voltage *U* = 18 V. The calorimeter contains 600 g of water, the sum of heat capacities of heat absorbing parts is 100 J $\mathrm{K}^{-1}$. The specific heat capacity of water: 4,18 J $\mathrm{g}^{-1}\mathrm{K}^{-1}$.
A6. Calculate first the heat capacity of calorimeter, $C_{\mathrm{k}}$.

$$C_{\mathrm{k}} = C_{\mathrm{v}} + C_{\mathrm{m}} = 600 \cdot 4{,}18 + 100 = 2608 \ \mathrm{JK}^{-1}$$

The heat supplied for the 2,2 °C increase

$$q = C_{\mathrm{k}} \Delta T = 5737{,}6 \ \mathrm{J}$$

The work done by electric heater:

$$q = w = \frac{U^2}{R} \cdot t \Rightarrow t = \frac{R \cdot w}{U^2} = \frac{24 \cdot 5737{,}6}{18^2} = 425 \ s$$