

A 7 Specific Heat of Solids

Task:

The mean specific heat of four substances between room T_2 and the boiling point of liquid nitrogen $T_1 = 77,5$ K shall be determined.

Theoretical background:

The heat required to increase the temperature of a solid at constant pressure by a small temperature interval ΔT can be calculated by

$$Q = \Delta H = n \cdot c_p \cdot \Delta T \quad (1)$$

Where n is the amount of substance of the solid and c_p the molar specific heat. The latter is a function of temperature $c_p(T)$ which for low temperatures can be explained by the theories of Einstein and Debye. At sufficiently high temperatures the Dulong-Petit rule applies, i.e. $c_p(T)$ can be roughly approximated by $3R$ for single and $6R$ for double atomic solids. In this experiment various solids are cooled down from a temperature T_2 to the boiling point of liquid nitrogen.

The mean molar specific heat between T_2 and T_1 will be referred to as \bar{c}_p . The heat transferred in this way can be calculated by:

$$\Delta H = H(T_2) - H(T_1) = n \cdot \int_{T_1}^{T_2} c_p dT = n \cdot \bar{c}_p \cdot (T_2 - T_1) \quad (2)$$

It causes the evaporation of Δn mol nitrogen N_2 with the vaporization enthalpy ΔH_{N_2} . Then

\bar{c}_p is determined from the experimental data by

$$\bar{c}_p = \frac{\Delta n_{N_2} \cdot \Delta H_{N_2}}{n \cdot (T_2 - T_1)} \quad (3)$$

Experimental realization:

Before starting the experiment a sufficient amount of each solid has to be crushed by a gripper (if necessary). In the next step the apparatus has to be assembled according to the scheme shown in Fig. 1 (without filling in nitrogen yet). N.b.: the narrowing zone in the neck is smaller than the diameter of the sample holder, so mind the sample sizes. The setup should be inspected before use by the advisor. In the next step advisor the vaporization calorimeter has to be filled at least to a half with liquid nitrogen under supervision of the advisor. Following that, the small Dewar is filled until the liquid encloses the neck of the calorimeter. This height has to be maintained throughout the entire experiment. [1]

Before a measurement is started, the evaporation rate should not be higher than 1-2 bubbles per second. This level can be influenced by varying the immersion depth of the calorimeter in the liquid nitrogen.

The sample preparation begins by weighing the crushed solid (max. load 20 g, and set **g** instead of **gn** (grain)). First an open topped vessel has to be tared and subsequently a certain amount of the sample has to be weighed (120 mg for each solid, except for Al, there only 80 mg). The height of the water column has to be determined by measuring the distance between the bulb scale and the water surface. Now the sample holder has to be installed and starting from t_0 the height of the vapor column has to be readout and noted with a frequency of one point per 10 seconds. [2]

Since nitrogen evaporates to a certain extent even without a sample, a preexperimental period of at least 5 data points has to be acquired. Then the grains are thrown into the calorimeter carefully without interrupting the measurement. After the evaporation has calmed down a final period of again at least 5 data points has to be acquired. The resulting curve corresponds to the one shown in Fig. 2.

For each substance two series have to be acquired. [3]

After the experiment the calorimeter is removed from the Dewar. As soon as it has thawed the metal grains are disposed in the local jar.

Here several questions which have to be answered immediately after assembling the apparatus:

- (1) Which consequences are expected after performing pronounced modifications of the experimental setup?
- (2) Which step (event) triggers the measurement (t_0 in Fig. 2)
- (3) Is the following statement correct? The content of the evaporation calorimeter should be removed within the time period in between two subsequent measurements.

Operational safety

It is necessary to protect the eyes by safety goggles!

When inside the evaporation calorimeter the pressure sinks below the environmental pressure and the water starts move slowly through the flexible tube towards the neck, you have to immediately remove the Dewar and pay attention that no water can penetrate the region of the liquid nitrogen.

Questions concerning the safety conditions

What is the reason for the sudden creation of a pressure lower than in the environment in the evaporation calorimeter?

What happens when water reaches the liquid nitrogen in evaporation calorimeter?

Data Analysis:

1. Calculate the partial pressure of nitrogen p_{N_2} for each data point using the equilibrium:

$$p_{air} = p_{N_2} + p_{H_2O} + p_{hydr.} \quad (4)$$

The environmental pressure can be acquired using the local barometer, for the vapor pressure of water use the approximate value at 293 K: $p_{H_2O} = 17,5$ Torr. The hydrostatic pressure correction can be calculated by:

$$p_{hydr.} = \rho_{H_2O} \cdot g \cdot h \quad (5)$$

ρ_{H_2O} can be set 1 g/cm^3 , $g = 9,81 \text{ m/s}^2$.

Calculate n_{N_2} for each data point using the ideal gas state equation from the calculated pressures and the measured volumes.

2. Use the graphical area compensation procedure (Origin description below) to determine the evaporated amount of Δn_{N_2} . Do not conduct the procedure with pen&paper.
3. Use equation (3) to calculate \bar{c}_p .

$$\Delta H_{N_2} = 5,56 \text{ kJ/mol}$$

Atomic and molecular weights of Zn, Sn, Al, KBr can be gathered from proper physical chemistry tables.

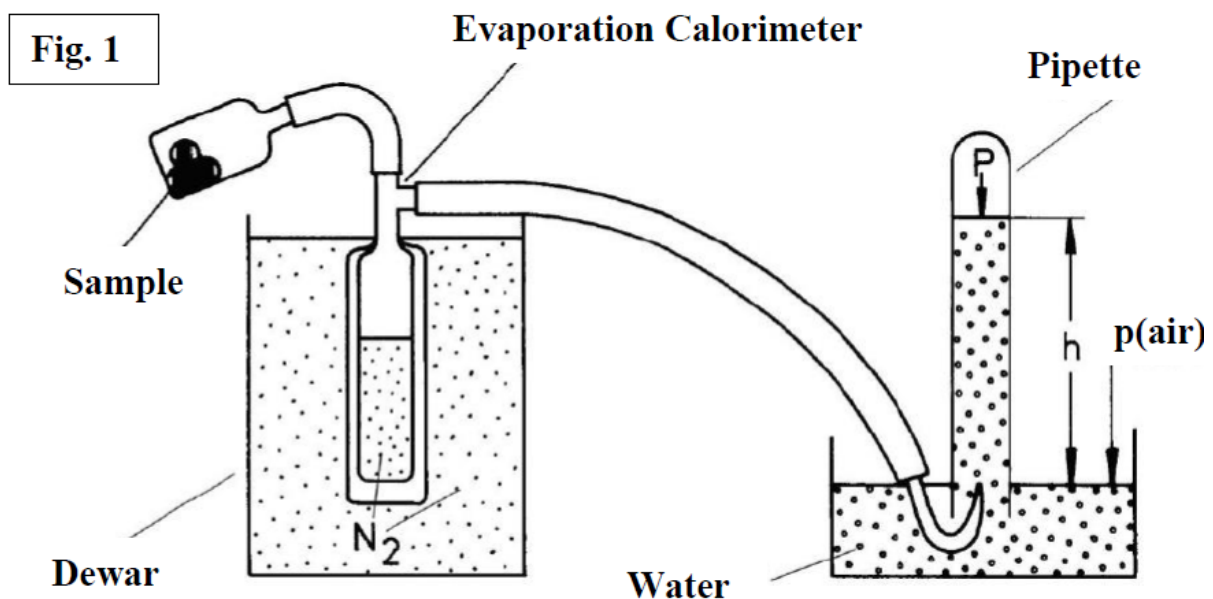
4. Interpret the results and compare to the rule of Dulong-Petit.
5. Discuss possible errors of the measurement procedure and estimate the error of the resulting values.


Required knowledge:

Definition of thermodynamic functions, definitions of c_p and c_v ; fundamental theorems of thermodynamics; definition of degrees of freedom and their contributions to c_p and c_v for gases, c_p of solids and metals; principles of the theories of Einstein and Debye; T^3 rule, comparison to Einstein/Debye; rule of Dulong and Petit; definition and *statistical* interpretation of entropy; state functions at low temperatures.

Additional questions:

1. Compare and interpret c_p of Al and Sn at low temperatures.
2. Discuss methods to reach low temperatures (especially adiabatic demagnetization)?
3. Discuss ΔH , ΔV , c_p , ΔS , ΔG for phase transitions at first and second order.

**Area compensation procedure using Origin 8.5G or newer:**


1. Plot n_{N_2} vs. Time in a point diagram.
2. Select the data points for the pre- and postexperimental periods using the button  (left symbol strip, fix by double click after selection) and determine regression lines for both periods.

3. Calculate the differences (measured data-preexp. regression line) and (postexp. Regression line-measured data) in the data book. (*Mark empty column/ click right/ set column values/ enter function/OK*).

Example: Let a be the slope and b the intersect of your preexperimental regression; your calculated nitrogen amounts can be found in column B, the times in column A. Then your function will be: $\text{col(B)} - (a \cdot \text{col(A)} + b)$

For the postexperimental period the subtraction must be conducted the other way round.

4. Plot both new data sets vs. T and integrate them (*Analysis / Mathematics/ Integration*).

Choose the integration areas with . The result of this integration can be found as an additional column in your data point table.

5. Calculate the difference between the last value of the integral column of the postexperimental period and the values of that same column in a new column.

6. Plot this difference function and the integral for the preexperimental period as shown in Fig.. 2b. Calculate the difference between both regression lines at the intersection time t_{sub} , this is your desired amount Δn_{N_2} .

Both diagrams have to be included in the protocol!

Fig. 2a:

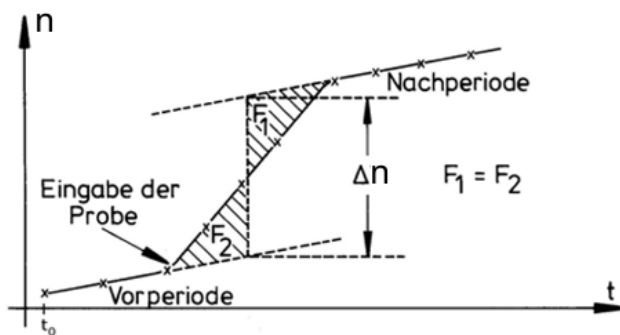
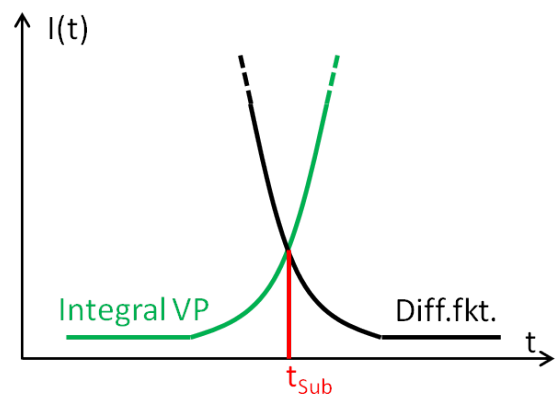


Fig. 2b:



Error analysis

The data obtained here result from single measurements which from time reasons could not be repeated frequently enough to apply statistical methods for error estimations. Consequently an easy estimation of the rough errors is sufficient in this experiment. When including the directly dependent quantities the errors can be calculated by exploiting the following formula

$$\Delta c_p = \left| \frac{\partial c_p}{\partial (\Delta n_{N_2})} \right| \Delta (\Delta n_{N_2}) + \left| \frac{\partial c_p}{\partial (n)} \right| \Delta n + \left| \frac{\partial c_p}{\partial (T_2)} \right| \Delta T_2$$

ΔT_2 is given by the accuracy of the thermometer, Δn can be approximated by the accuracy of the weighing machine. The error of the N_2 content, $\Delta(\Delta n(N_2))$ can be estimated by estimating reasonable errors for determination of the volume (give reasons for your choice).