

Handout

Thermometer calibration (exp. 02.)

Important concepts

Working principles of mercury thermometer (MT), error sources of MT, calibrating equilibrium systems, boiling point of a liquid, sensitivity of MT, stem correction, correction value for MT.

Objective

You will calibrate a mercury thermometer by immersing it in different equilibrium systems of known equilibrium temperatures.

Mercury thermometer

Working principle of mercury thermometers are based upon the difference between the thermal expansion coefficient of liquid mercury (about $1.8 \cdot 10^{-4} \text{ K}^{-1}$) and glass (about $0.2 \cdot 10^{-4} \text{ K}^{-1}$).

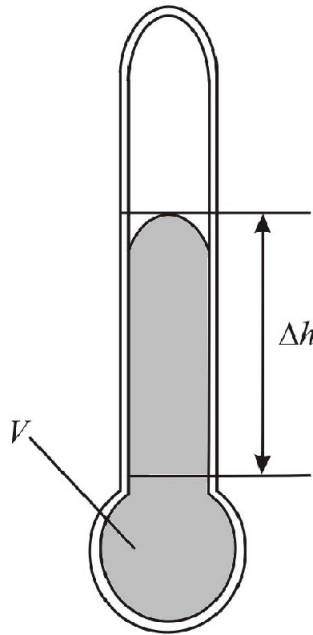


Fig. 1. Mercury thermometer.

Thermometer design is a relatively simple matter. The main parts, the bulb and capillary are made of glass. At a reference temperature most of the liquid with volume V_0 takes place in the bulb (i.e. mercury container). The diameter of capillary should be uniform throughout the length graded.

The sensitivity of mercury thermometer clearly depends on three factors: β , the difference of the cubical expansion coefficients of the liquid and glass, the volume of liquid at temperature T and r , the capillary radius.

$$\frac{dV}{dT} = \beta \cdot V_0$$

where V can be replaced by the height of mercury, h

$$V = r^2\pi \cdot h \quad \text{and} \quad dV = r^2\pi \cdot dh$$

therefore the sensitivity

$$\frac{dh}{dT} = \frac{\beta \cdot V_0}{r^2\pi} \quad \text{for finite changes :} \quad \frac{\Delta h}{\Delta T} = \frac{\beta \cdot V_0}{r^2\pi}$$

is directly proportional to β and V_0 . The smaller the radius of capillary the higher the expansion of mercury thread on unit change of temperature. The capillary is usually marked at two points (say at 0 °C and 100 °C) and graduated uniformly in between, on an assumption that the volume of a fixed mass of mercury is a linear function of temperature.

Thermometers are not affected by vapour pressure above the capillary column, as a barometer would be. It is only necessary that the liquid be clearly distinguishable from the volume above the liquid. The glass capillary magnifies the column, and can be shaped to increase the magnification.

Mercury has $\beta = 0.181 \times 10^{-3}$ per °C, while ordinary soda-lime glass has $\beta = 0.0276 \times 10^{-3}$ per °C. The β of most liquids is on the order of 10^{-3} , while that of most solids is about 10^{-5} , so the solid expansion is only about 1% of that of the liquid. For mercury, the difference is $\beta' = 0.153 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$. Suppose our thermometer has $V = 250 \text{ mm}^3$, with a capillary bore of 0.2 mm. The sensitivity will be $dx/dT = 1.22 \text{ mm}/^\circ\text{C}$, so a scale reading from -10°C to 110°C will be 158 mm long. This is actually fairly typical of small mercury thermometers. Mercury melts at -38.87°C , and boils at 356.7°C , so it is useful over a wide range. A mercury column is also very easily seen.

Sources of error

There are some important sources of error in measuring with mercury thermometer.

1. The glass capillary that contains the mercury thread is never quite even in diameter along its whole length as it should be.
2. Glass not being crystalline material, cannot adjust its volume promptly to an abrupt drop in temperature. Consequently when you transfer a thermometer from boiling water to ice/water bath mercury thermometers tend to show lower than 0 °C for the melting point of ice. This type of error is called the **zero point depression**.
3. Thermometers are normally scaled on the assumption that when a reading is done, the whole thermometer is in thermal equilibrium with its surroundings. In practice however we only immerse the bulb and a part of capillary in what we want to take the reading of, and therefore part of the thread is practically exposed to room temperature. If the thread temperature is significantly different from that of the bulb we need to take a **stem correction**.

It can be easily seen from the above mentioned errors that for precise measurements the thermometer should be calibrated. To obtain proper temperature values we define the correction, ΔT

$$\Delta T = T_e - T_m \tag{1}$$

where T_e is exact (correct) temperature established by phase equilibria and T_m means the measured one.

Rearranging this expression,

$$T_e = T_m + \Delta T \quad 1a.$$

from 1a. is shown that one gets the correct temperature by addition of ΔT to the measured. The value of ΔT can be either negative or positive number.

Measuring the temperatures of some equilibrium systems with well known temperatures you can plot the ΔT vs. T_m in the 0 – 100 °C range.

Procedure

To measure the calibration curve check your thermometer with the following systems:

1. Ice/water equilibrium system at a pressure of $1.013 \cdot 10^5$ Pa denotes 0.00 °C.
2. $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, solid/liquid equilibrium system. The phase equilibrium is set by the following process, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}(s) \leftrightarrow \text{Na}_2\text{SO}_4(s) + \text{Na}_2\text{SO}_4(\text{aqueous solution})$, i.e. between solid $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}(s)$ and its saturated solution.

To do this take a clean and dry test tube, place a glass stirrer into it and fill it up to about two-third with solid salt (the salt should be properly ground in a mortar beforehand). Heat it gently over a Bunsen burner at constant stirring until about half of the salt is melted away. Then immerse your thermometer into the mixture and put it into another glass tube (thermal insulator). After that the whole apparatus together with its holder should be placed into a beaker containing water the temperature of which should be about 32 °C (to thermostat the system).

Why should you use dry test tube for melting one part of the solid $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$?

3. When finishing step 2 immerse the thermometer into a thermostat liquid, this thermostat produces a constant temperature at about 27 °C. Allow some time the thermometer to equilibrate, and take several readings of temperature of thermostat liquid. The same procedure should be repeated in an other thermostat produces a constant temperature at about 37 °C.
4. Boiling water/water vapour. Setting a boiling point *about* 100 °C depending on the atmospheric pressure. In order to calculate the equilibrium boiling temperature in the latter case you will have to determine the atmospheric pressure by reading a barometer and the thermometer attached to it. First read the upper mercury level of Torricelli's tube in mmHg, than the lower level of mercury and the temperature. Since a given difference between the mercury columns of the barometer represents different pressures at different temperatures owing to the temperature dependence of mercury density you have to "reduce" this difference by giving its value at the standard temperature of 0 °C.

$$p_0 = p - 0.125 \cdot T \quad 2.$$

In Equation 2 p_0 is the pressure at 0 °C, p is the measured pressure (both are given in mmHg) and T is the temperature of measurement.

The value of p_0 is given in Pa instead of mmHg, so

$$p_0^1 = 133.32 \cdot p_0 \quad 3.$$

The boiling point, T_b of water can be given in centigrade as a linear function of pressure

$$T_b = 100 + (p_0^1 - 101325) \cdot 2.75 \cdot 10^{-4} \quad 4.$$

5. Stem correction. Draw out some part of the thermometer body above the upper cork level, so that a certain length, say 50 – 60 °C, of the thread will remain outside the mantle, and note it. That length will be referred to as stem length, l in centigrade. (E.g. the thermometer is drawn up to 55 °C and the mercury thread is at 99,60 °C so the stem length is 44.6 °C.) Attach another thermometer in the middle point of the stem and note its temperature T_{stem} . From the following formula you can calculate the stem correction. ΔT_{stem} :

$$\Delta T_{\text{stem}} = l \cdot (T - T_{\text{stem}}) \cdot 1.6 \cdot 10^{-4} \quad 5.$$

where T is the temperature read from the thermometer under calibration. You must compare the ΔT_{stem} value calculated from Eq. 5 with the one obtained from the difference between the measured boiling points with thermometer totally in the mantle ($T_{b,m}$) and some part is drawn out of it ($T_{b,s}$) respectively. This will be your measured $\Delta T_{\text{stem, meas}}$.

6. Zero point depression. To measure this, remove the hot thermometer from the steam mantle and place immediately in the ice/water mixture. (The thermometer will not break owing to this temperature drop.)

Apparatus

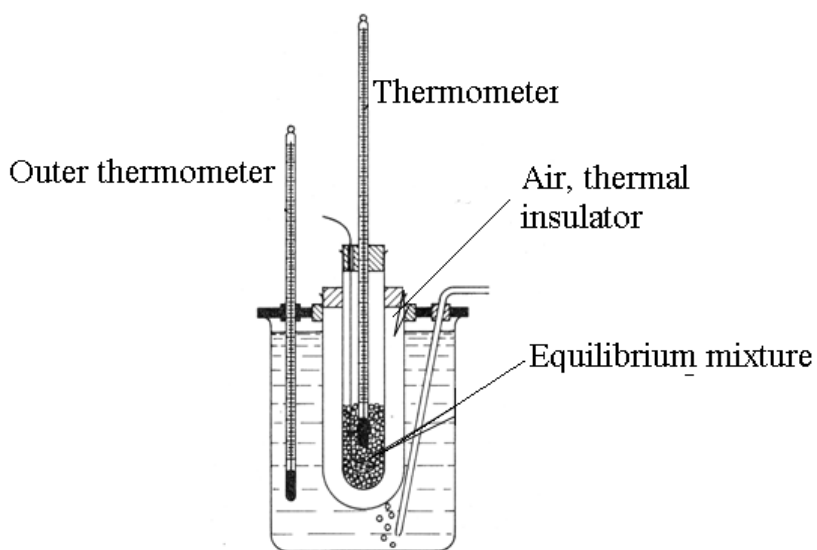


Figure 2. Apparatus for the determination of equilibrium temperature in the $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, solid/liquid equilibrium system.

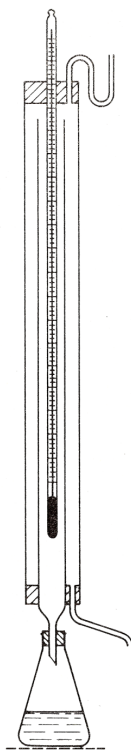


Figure 3. Apparatus for the determination of equilibrium temperature in the water liquid/vapour equilibrium system.

Calculation

For the calibration diagram of thermometer

In ice/water mixture

$$\Delta T_1 = 0^\circ\text{C} - T_{m,1}$$

In $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, solid/liquid equilibrium system,

$$\Delta T_2 = 32,38^\circ\text{C} - T_{m,2}$$

For boiling point correction calculate the boiling point of water using Equations 2, 3, 4.

$$\Delta T_3 = T_b - T_{m,3}$$

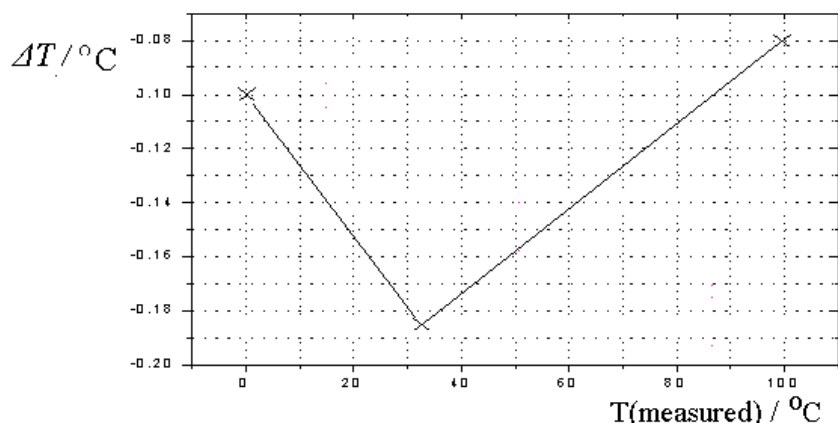
For zero point depression, T_d take the difference between measurement 1 and measurement 6. At measurement 6. use the minimum temperature.

$$T_d = T_{m,1} - T_{\min,6}$$

To measurement 3.

From calibration diagram you prepared, read the value of ΔT belonging to the measured temperatures observed in thermostats and give the correct temperature (T_c) values.

Example calibration curve



Graphs, results, data to be reported

1. Calculate the boiling point of water using Equations 2, 3, 4.
2. Calculate the three ΔT values and plot the ΔT vs T_m graph.
3. Calculate the correct temperature of the thermostats by using the graph (point 2.) and Eq. 1a.
4. Calculate T_{stem} using Eq. 5, and $\Delta T_{\text{stem, meas}}$ and zero point depression.

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. It is also the material of pre-lab questions.

MLT Q and A

Q1. Define the volumetric thermal expansion coefficient.

A1. The initial volume of a liquid is V_0 at a temperature T_0 , and its final volume is V at a temperature T , then the *change in volume* of the liquid, $\Delta V = V_0 - V$, is given by

$$\Delta V = \beta \cdot V_0 \cdot \Delta T$$

where $\Delta T = T_0 - T$ is the change in temperature of the object, and β (in $^{\circ}\text{C}^{-1}$) is a constant which is characteristic of the material of which the object is made, called the *coefficient of volumetric expansion*.

Q1.1 What is the working principle of mercury thermometer?

A1.1 The mercury thread changes its height moving in a glass capillary answering the temperature change in its surroundings. There is a great difference in between the volumetric thermal expansion coefficient of mercury and glass. This difference makes possible to observe the response of mercury thread to a thermal change in its surroundings.

Q2. Decide which is the greater sensitivity of the two mercury thermometers? All parameters of thermometers are the same, but the capillary radius are $r_1 = 0,1$ mm and $r_2 = 0,05$ mm.

A2. The sensitivity, S can be given as

$$S = \frac{\Delta V}{\Delta T} = \beta \cdot V_0$$

When internal diameter of capillary is even and stem height, h is changed exclusively with temperature

$$S = \frac{\Delta h \cdot r^2 \cdot \pi}{\Delta T} = \beta \cdot V_0 \quad \text{Rearranging: } S = \frac{\Delta h \cdot \beta \cdot V_0}{\Delta T \cdot r^2 \cdot \pi}$$

The thermometer with smaller radius ($r_2 = 0,05$ mm) has higher sensitivity.

Q3. Set out and characterize the calibrating mixtures used!

A3. They are binary systems in thermodynamic equilibrium producing a certain temperature. Ice water two phase system shows 0°C , $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ solid/liquid system shows 32.38°C , which can be taken as independent of external pressure. While a boiling liquid water/vapour water system has an external pressure dependent boiling point. They can be applicable for calibrating a thermometer in the range $0 - 100^\circ\text{C}$.

Q4. Define stem correction.

A4. Stem is a certain length of mercury thread outside the measuring system. The stem part has lower temperature than the bulb, as a result, thermometer shows lower temperature. By measuring the stem length, stem temperature and the temperature of thermometer to be calibrated stem correction can be calculated by formula.

Q5. How can you calculate the values for *correction*, Δ ?

A5. The difference between the correct (set by equilibrium system) and measured temperature gives the value of correction, Δ . The correction can have negative or positive value.

Q6. What data are taken from barometer?

A6. The upper and lower levels of mercury meniscus in mmHg, and the temperature of barometer body. The mercury level difference shows the external pressure uncorrected. You should correct it to 0°C the temperature where scale has been calibrated.

Q7. Give definition for boiling point.

A7. The temperature at which the vapour pressure of boiling liquid is equal to the external pressure is called the boiling temperature or boiling point.