1.9. DETERMINATION OF THE VAPOUR PRESSURE OF A PURE LIQUID SUBSTANCE BY THE „SIMPLE STATIC METHOD” AS A FUNCTION OF TEMPERATURE. DETERMINATION OF THE ENTHALPY CHANGE OF EVAPORATION.

The necessary theoretical background:

- *thermodynamic condition of phase equilibrium,*
- *Gibbs’s phase rule (definitions of component, phase and degree of freedom),*
- *phase diagram of pure substances: melting point, triple point, boiling point,*
- *critical temperature (phase diagram of water),*
- *Clapeyron equation,*
- *Clausius – Clapeyron equation.*

You can find theoretical information in English in *Atkins’ Physical Chemistry, Oxford University Press; 10th Revised edition (March 20, 2014).* In addition to the above-mentioned theoretical background and the detailed description below, further information on the vapour pressure measurements can be obtained in Chapters 1.5.4.1., 1.5.7.1. and 1.5.7.2. of “*Farkas József, Kaposi Olivér, Mihályi László, Mika József, Riedel Miklós, Bevezetés a fizikai kémiai mérésekbe, Vol. I, Tankönyvkiadó Budapest, 1988 (in Hung.)”*, as well as in *“Szalma József, Láng Győző, Péter László, Alapvető fizikai kémiai mérések és a kísérleti adatok feldolgozása (introduction of Chapter 6. and Sub-chapter 6.1., pages 123 to 131, in Hung.)”*. Though this description below is a full description of the measurement, it does not include all necessary theoretical information.

Necessary measurement-technical knowledge:

- *measurement of pressure by mercury manometer (U-tube),*
- *measurement of open air pressure by mercury barometer,*
- *measurement of pressure by piezoresistive digital vacuum meter (Appendix 1),*
- *measurement of open air pressure by piezoresistive digital barometer (Appendix 1).*

I. TEMPERATURE DEPENDENCE OF VAPOUR PRESSURE. THEORETICAL INTRODUCTION.

A type of the one-component, two-phase equilibriums is the liquid-vapour equilibrium. According to the Gibbs’s phase rule such system has one degree of freedom: at a definite temperature the vapour is in equilibrium with the liquid at a certain pressure. This pressure is called equilibrium vapour pressure. Conversely, only one temperature (equilibrium temperature) belongs to a maintained definite pressure. The temperature dependence of the vapour pressure is described by the *Clausius - Clapeyron - equation* as follows:

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{RT^2} \qquad \textbf{(1)}$$

where *p* and $\Delta_{\mathrm{vap}}H$ denote the equilibrium vapour pressure and the molar enthalpy change of evaporation (molar heat of evaporation), respectively. *T* and *R* denote the temperature and the gas constant, respectively.

By integrating Eqn. (1) and by neglecting the temperature dependence of the enthalpy change of evaporation, we obtain the following equation:

$$\ln p = -\frac{\Delta_{\mathrm{vap}}H}{R} \cdot \frac{1}{T} + A \qquad \textbf{(2)}$$

where A is a constant. It can be seen that the vapour pressure depends on temperature exponentially:

$$p = B \cdot \exp\left(-\frac{\Delta_{\text{vap}} H}{RT}\right) \qquad \textbf{(3)}$$

where $B = e^{A}$. To determine the molar enthalpy change of evaporation, Eqn. (2) is used. Based on Eqn. (2), if the vapour pressure is measured at several temperatures and we plot $\ln p$ vs. 1/T, the value of $\Delta_{\text{vap}} H$ can be calculated from the slope of the fitted straight line as follows:

$$m = \frac{\mathrm{d}[\ln p]}{\mathrm{d}\left[\frac{1}{T}\right]} = -\frac{\Delta_{\text{vap}} H}{R} \qquad \textbf{(4)}$$

Therefore: $\Delta_{\text{vap}} H = -m \cdot R \quad (\text{J/mol})$. where $R = 8.3143 \quad \text{J/(mol K)}$.

Important remark:

We cannot apply the simple static method at temperatures higher than room temperature, because we maintain the temperature of the round-bottom flask that contains the sample. The other parts of the equipment are at room temperature. Furthermore, the equilibrium vapour pressure is determined by the coldest place of the closed space where the liquid sample and its vapour is situated. If the manometer (vacuum meter) is situated at room temperature, we cannot measure over the room temperature since the latter will be the coldest point of the apparatus. If we would like to measure vapour pressures at higher temperatures than room temperature we should maintain the temperature of the whole apparatus at the controlled temperature. Nevertheless, we measure vapour pressure only below the room temperature.

II. MEASUREMENT AND CALCULATION TASK:

- **measurement of vapour pressure of an organic solvent (mostly diethyl ether) at 4-5 different temperatures by the simple static method,**
- **calculation of the molar enthalpy change of evaporation from the obtained temperature – vapour pressure data-pairs according to the Clausius – Clapeyron equation.**

Measuring equipment:

The picture of the measuring equipment can be seen in Fig. 1.

Equipments, chemicals

In addition to the apparatus presented in Fig. 1, it is necessary:

- 1 Bunsen stand;

- 2 water aspirator pump;

- 1 buffer bottle;

- 1 beaker (600 cm^3 equipped with thermal isolation) to make freezing mixtures;

- 1 beaker with two pipe-ends to maintain the temperature by means of the flowing tap-water

- 2 vacuum rubber tubes;

- 2 rubber tubes;

- 1 bent metal rod to stir the tempering bath;

- sample (an organic solvent);
- 1 funnel to load the solvent
- crushed ice;
- NaCl (technical quality to make freezing mixtures);
- 1 barometer.

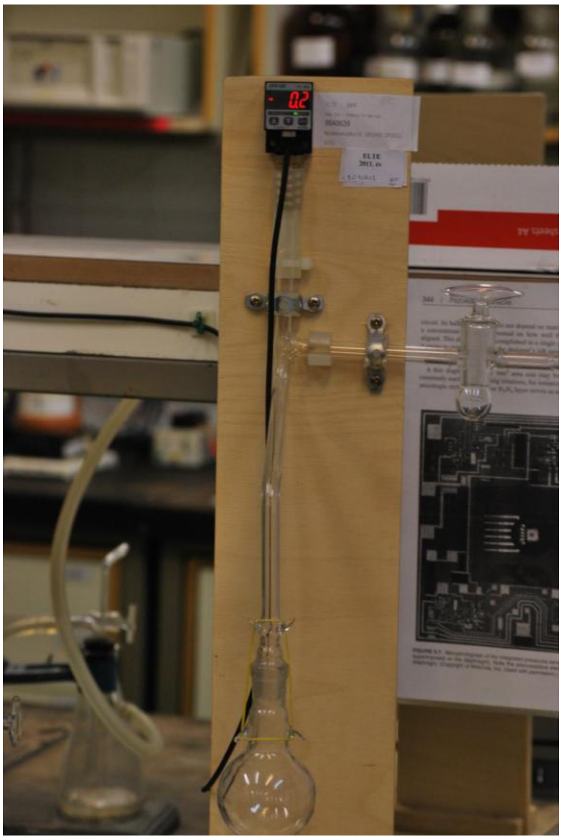


Fig. 1
Equipment for the measurement of vapour pressure by the static method

III. EXECUTION OF THE MEASUREMENT

Constructing and evacuating the measuring equipment.

In case of open apparatus the digital vacuum meter should display 0. If the vacuum meter displays a different value, it should be calibrated. This operation should be done exclusively by the professor.

The ground-glass joints of the round-bottom flask and the glass tube connecting the vacuum meter should be cleaned. **The round-bottom flask must not be cleaned by water either before or after the measurement,** because the evaporation of the residual water increases the pressure and therefore falsify the measured data! After cleaning the ground-glass joints of the round bottom flask and the connecting glass tube from dust lubricate them thinly with vacuum grease! Connect the flask to the glass tube and rotate the joints in order to lubricate the whole surface of the joints for better sealing! Then remove the flask from the connecting glass tube again and load approximately the half of the flask with the sample (diethyl ether) through the plastic funnel! Match the joints again and fasten them by means of two rubber rings! Finally place the flask in a room-temperature water bath! Connect the bypass tube of the water aspirator pump to the equipment across the buffer bottle! For this manipulation, please ask for the help of the professor! Place the round-bottom flask in a beaker containing a **room-temperature-water-bath** so that the level of the water bath to be higher than the level of the liquid sample! **Use safety glasses during the whole measurement! The diethyl ether is flammable and toxic, handle it with care! After use (at the end of the measurement) pour the sample into the collecting bottle!**

Open the tap of the aspirator vacuum pump then close the air inlet valve on the buffer bottle! Slowly open the closed valve that separates the sample holder and the vacuum meter from the pumping system and keep it open for maximum 4-5 seconds! When the pressure inside the apparatus becomes approximately constant, close the valve! It is not recommended to keep the valve open for longer time since the sample evaporates from the flask. Wait until the pressure inside the apparatus does not grow fast any more. Then pump the system again! Repeat this operation 4-5 times or even more until the system does not contain residual air! The air-free condition can be checked at constant bath-temperature by comparing the pressure difference data before and after a new evacuating step. If the pressure data do not show a downward trend the apparatus is air-free.

After removing the air from the apparatus, it is not necessary to keep the water aspirator pump on. In order to switch off the pump keep the separating valve closed, open the air inlet valve on the buffer bottle then close the tap water! (This way we can avoid the backflow of the tap-water into the buffer bottle and the system.) In this stage we can start recording the temperature and pressure difference data.

Detection of the vapour pressure data

Set the temperature of the bath to be lower than the temperature of the environment, otherwise the evaporating sample condenses at the colder parts of the apparatus and the vapour pressure will be determined by the coldest part of the system. Stir the bath quite often using the bent metal rod in order to avoid any temperature gradient! The temperature of the bath is measured by a mercury thermometer immersing in the bath. **Record the values of temperature and pressure difference in each minute or two minutes even if the data do not change (at least for some time more)! Appendix 2 includes a blank table, print it in A4 format and bring it with you to the lab! You will record the data in this table!** The vacuum meter displays the difference of the inner and outer pressure data. **Continue recording the data until the data do not change (i.e. equilibrium is reached)!** The equilibrium state should clearly be seen from the recorded data. **Instead of averaging the recorded (ϑ, Δp_m) data we use the final equilibrium (ϑ, Δp_m) data for the evaluation.** The other (ϑ, Δp_m) data-pairs will not be used for the evaluation. If the (absolute value) of the pressure difference decreases at a constant bath temperature continuously without any tendency to stop, the system is not sealed sufficiently. In this case the joints should be better sealed by cleaning and re-lubricating them and the whole evacuation procedure should be repeated.

The next measurement should be performed at the **temperature of the flowing tap-water**. This operation can be realised by using a special beaker having two pipe-ends, the one at the bottom, the other at the top of the beaker. The lower pipe-end should be connected to the tap, the upper one to the water aspirator pump so that the pumping speed should be higher than the influx speed, otherwise the water overflows. This way a constant level of the water can be adjusted and the overflow can be avoided. **The temperature and the pressure difference data should be recorded the same way as mentioned above**.

The next temperature will be 0 ^{o}C. For this purpose make a crushed ice - distilled water freezing mixture in the beaker, that you previously used for the measurement at room temperature. The ice particles should be really small. To make the crushed ice an ice crusher is available. The mixture should be fluid and the relative amount of the ice should be large enough in order to prevent floating of the ice particles on the surface of the liquid. The freezing mixture should be frequently stirred by using the bent metal rod. **The temperature and the pressure difference data should be recorded the same way as mentioned above**.

The next temperatures will be below 0 ^{o}C. Adding NaCl (technical quality) to fresh crushed ice the eutectic temperature (-19 °C) of the NaCl – H_2O system can be reached theoretically. Nevertheless, due to the bad thermal isolation of the beaker this temperature cannot be reached easily. However, around –10 °C can be easily reached and stabilised. Make measurements at two temperatures in the **0 – –10 °C temperature range first at around –5 °C, then at around –10 °C!** In order to assure the latter temperature, add more salt to the mixture but first make measurements at the higher temperature! This will be the fourth and the fifth data series. Add the salt in small portions to the ice and stir the mixture continuously! After reaching the minimum temperature perform the measurement the same way as previously at the three other temperatures (see above)! Frequently stir the liquid even during reading the (ϑ, Δp_m) data otherwise a temperature gradient is formed in the freezing mixture! If you cannot stabilise the temperature please ask for the help of the professor! The professor will help in selecting the final data from the data-set as well! If there is some time more, make a measurement even at the eutectic temperature! In order to reach this temperature, start from ice and salt (without water) and stir/mix them to reach the eutectic temperature!

At the end of the measurements you will have 5-6 final (equilibrium) (ϑ, Δp_m) data-pairs. Do not forget to measure the open air pressure using the digital barometer!

IV. EVALUATION OF THE MEASURED DATA

1. We should know the open air pressure (p_{out}) for the evaluation of the measurement. This value can be read from the digital barometer. The device can be required from the technician. Remember, the device displays the air pressure value in hPa (resolution: 0.1 hPa)! (Nevertheless, the vacuum meter displays the pressure difference (Δp_{diff}) in kPa (resolution: 0.1 kPa)).

2. The temperature data displayed by the mercury thermometer should be corrected since they are not absolutely precise. If the displayed apparent temperature of the ice – water equilibrium freezing mixture was *e.g.* 0.5 ^{o}C instead of the theoretical 0 ^{o}C, then all temperature values should be corrected with –0.5 ^{o}C before further calculations are performed. Using this correction method we assume an additive (constant) correction although this latter is not necessarily true since the inner diameter of the capillary tube is not absolutely the same along the whole tube.

3. Recalculate both pressure data (p_{out} and Δp_{diff}) into a common unit (*e.g.* Pa) and calculate the vapour pressure (p) according to the following equation:

   $$p = p_{\mathrm{out.}} + \Delta p_{\mathrm{diff}} \qquad \textbf{(5)}$$

   (Remember that the vacuum meters operate at lower pressures than the outer air pressure and they display the difference between the inner and the outer pressures. Therefore the displayed pressure difference (Δp_{diff}) is a negative number if the vapour pressure of the sample (inner pressure) is lower than the outer air pressure. **Only the final, *i.e.* equilibrium temperature – vapour pressure data-pairs should be used for the further evaluations! This way we shall have 5 data-pairs!**

4. Plot the vapour pressure against the temperature using ORIGIN software! You will obtain the $p\,/\,\mathrm{Pa}$ *vs.* $\vartheta/{}^\circ\mathrm{C}$ plot as a discrete function!

5. For the determination of the enthalpy change of evaporation plot $\ln(p/\,\mathrm{Pa})$ against $T^{-1}\,/\,\mathrm{K}^{-1}$! Fit a straight line on the points by linear regression using the appropriate menu task! According to Eqn. (4) the value of $\Delta_{\mathrm{vap}}H$ can be obtained from the slope of the straight line. Copy the obtained statistical box to the figure sheet!

6. **Optional task**: return to the p/Pa *vs.* $\vartheta/{}^\circ\mathrm{C}$ plot! Do not fit any non-linear function for the points but adopt the values of the *A* and *B* parameters of equation $\ln(p) = A + B/T$, obtained from the linear regression (*see* Point 5 above) and draw the $p = e^{A+B/T} = e^{A+B/(\vartheta+273.15)}$ function using Graph / Add Function menu point of ORIGIN)! Type the equation as $p = \exp(A+B/(x+273.15))$ with your own *A* and *B* values! Only symbol *x* is accepted as independent variable (ϑ) during typing the equation! Make as many points of the curve as possible (*e.g.* 1000)! This way the functions obtained in Points 5 and 6 will be consistent with each other.

V. Data to submit:

- A **table** including the following quantities (only with the five final equilibrium data): $\vartheta/{}^\circ\mathrm{C}$ (4 decimals), T/K (5 decimals), T^{-1}/K^{-1} (5 decimals), $\Delta p_\mathrm{diff}/\mathrm{kPa}$, p/Pa (5 decimals), $\ln(p_\mathrm{g}/\mathrm{Pa})$ (5 decimals).

- The p/Pa *vs.* $\vartheta/{}^\circ\mathrm{C}$ function.

- The $\ln(p/\mathrm{Pa})$ *vs.* T^{-1}/K^{-1} function including the statistical window of the regression presenting the slope and intercept (at least in 6 decimals) and their standard deviations (at least in 4 decimals).

- The value of $\Delta_\mathrm{vap}H$ in kJ/mol with its uncertainty. An example of the calculation of the uncertainty can be seen below.

VI. EXAMPLE FOR THE CALCULATION OF THE HEAT OF EVAPORATION AND ITS UNCERTAINTY

The parameters of the regression are given by the ORIGIN in the statistical box (see the figures below). For example the slope, *m* = 3425.45 K, the standard deviation of the slope, *S*(*m*)= 16.32 K.

The slope together with its confidence interval is as follows:

$$m \pm t_\alpha \cdot S_\mathrm{m} = -(3425.45 \pm 3.18 \cdot 16.32) = -(3425.45 \pm 51.90)\,\mathrm{K}$$

(if 95% reliability is chosen, α = 5%. In case of *n* = 5 measured points the degree of freedom, $f = n-2 = 3$ and $t_\alpha^f = 3.18$.)

The calculation of the heat of evaporation according to Eqn. (4) is as follows:

$$m = -\frac{\Delta_\mathrm{vap}H}{R} \qquad \text{from which:} \qquad \Delta_\mathrm{vap}H = -R \cdot m$$

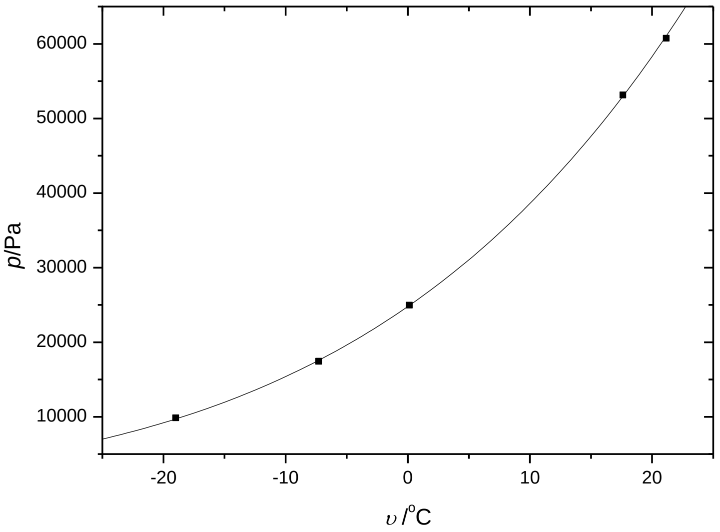
$$\Delta_\mathrm{vap}H = -R \cdot m = 8.3143 \cdot (3425.45 \pm 51.90) = (28480 \pm 431)\,\mathrm{J/mol}$$

<u>Before we present the final result, we have to round it according to its uncertainty!</u>

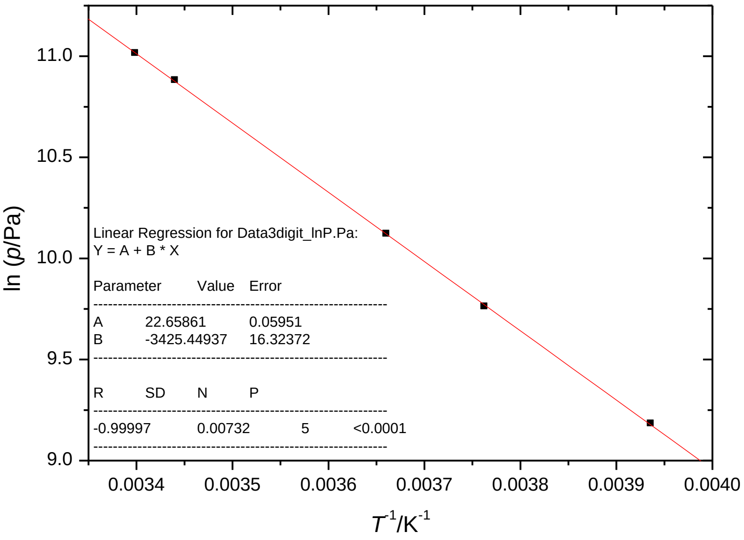
$$\underline{\Delta_\mathrm{vap}H} = (28480 \pm 430)\,\mathrm{J/mol} = \underline{(28.48 \pm 0.43)\,\mathrm{kJ/mol}}$$

VII. Sample figures to help to evaluate the measurement.

The vapour pressure as a function of temperature



The logarithm of the vapour pressure as a function of reciprocal of temperature



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Linear Regression for Data3digit_lnP.Pa:
Y = A + B * X

Parameter        Value    Error
------------------------------------------------------------
A          22.65861        0.05951
B          -3425.44937     16.32372
------------------------------------------------------------

R          SD          N          P
------------------------------------------------------------
-0.99997         0.00732          5          <0.0001
------------------------------------------------------------
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Appendix 1

Piezoelectric effect:

In a crystalline substance, an electric voltage is formed during a mechanical deformation. Fig. 4 shows that a mechanical deformation in the direction of the x-axis causes charge separation in the originally neutral silica crystal.

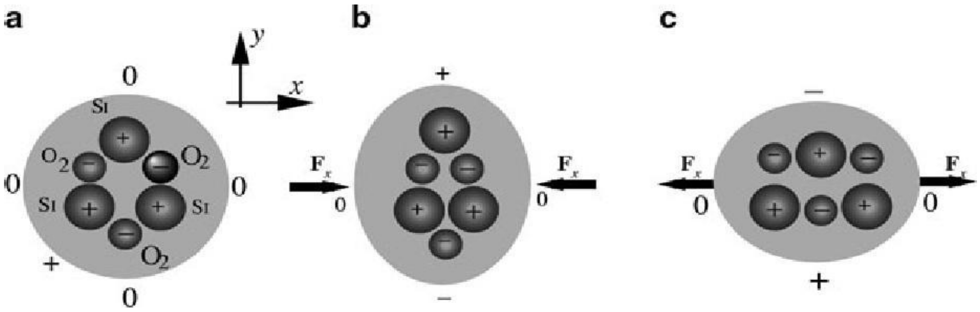

Fig. 4 Piezoelectric effect in the silica crystal (helix model according to A. Meissner [1]) [2]

Piezoresistive effect:

In case of a piezoresistive effect, a charge separation does not occur under mechanical stress, but the electric resistance of the material is changed. The single-crystal silicon is a good pressure converter, its deformability is ideal and it is perfectly elastic. The pressure sensor diaphragm is prepared by chemical etching (for example using KOH - H_2O or N_2H_4 – H_2O) and doping (e.g. by boron.). The thickness of a sensor formed from a *e.g*. 7x7 mm chip is 5 to 50 μm, depending on the pressure to be measured. The ideal thickness of the wafer is about 100 times of the thickness of the diaphragm.

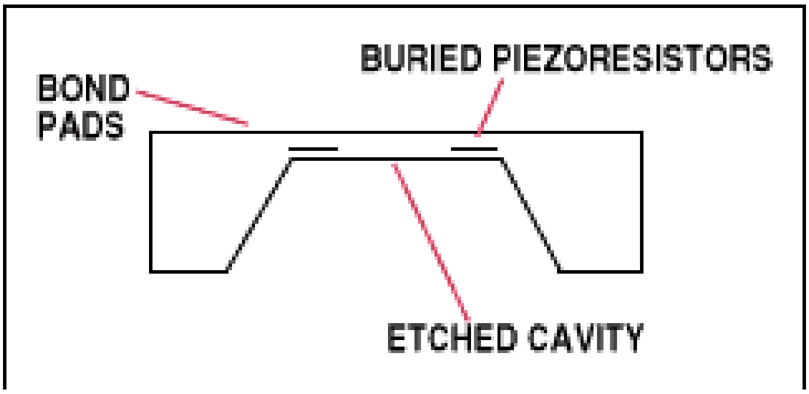

Fig. 5 Etched silicon chip

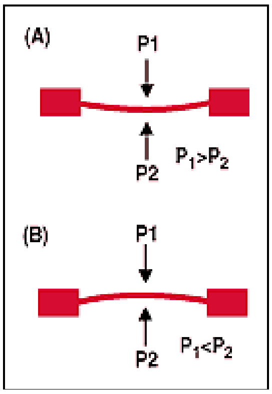

Fig. 6 Deformation of a diaphragm due to pressure difference

The deformation of the diaphragm depends on the pressure conditions. In Fig. 6a the reference pressure P2 is equal to some degree of vacuum (*e.g*. below 0.1 hPa or even better). In this case the device measures *absolute pressure*, and called as *barometer*. In Fig. 6B the P2 reference pressure may be *e.g*. the outside air pressure. In this case, the device called as *differential pressure gauge or vacuum gauge*. This is our present pressure sensor in the equipment. (The barometer is not a part of the measuring equipment, it is a separate device.) The piezoresistive effect is formed by ion implantation to make semiconducting resistors. The orientation of the resistors is so that two of them are parallel, another two are perpendicular to the appropriate crystal plane. For example, on a round disc-shaped diaphragm, the orientation of the resistors can be radial and tangential. The values of the resistances are almost equally increased or decreased, depending on the orientation, when applying the pressure difference. The resistors (2-2 radial and tangential) are often linked to Wheatstone bridge, which enables highly accurate resistance measurements via voltage measurement. Though the output signal is voltage but the instrument was calibrated to known pressure values so that the device directly displays pressures.

[1] Meissner A (1927) Über piezoelectrische Krystalle bei Hochfrequenz., Z Tech Phys 8:74.
[2] Jacob Fraden, Handbook of Modern Sensors, 4th Edition, Springer Science+Business Media, LLC 2010.

Appendix 2

Data-sheet to the measurement entitled „Determination of the vapour pressure of a pure liquid substance by the „simple static method” as a function of temperature – determination of the enthalpy change of evaporation

Name(s) of the student(s)____

Air pressure:________________________ Date:_____________________

υ / °C	Δp / kPa	υ / °C	Δp / kPa	υ / °C	Δp / kPa

Δp is the pressure difference displayed by the vacuum meter.