

6 BOILING POINT OF LIQUIDS AND MELTING POINT OF SOLID MATERIALS

Theory

In a solid material the atom, ions, molecules are bound tightly on their places, they can vibrate only around their equilibrium position, but do not perform translational motions. The solid materials have defined shape and volume. With increasing temperature, the energy of the material components increases and at the melting point they release their position. The solid material becomes a liquid. In liquids the atoms, ions or molecules are bound less tightly than in solids. They can perform vibrational, translational and rotational motions, however, there are weakly connected to their neighbours. They form a surface, also. The volume of a liquid depends on its density, but its shape depends on the shape of the container, where it is placed. Increasing the temperature of a liquid, the molecules of the liquid releases its surface and evaporates, become a gas. In a gaseous material, particles are moving randomly in the whole volume of the container, affecting each other only slightly, (in an ideal gas do not affect at all), except the moments of collisions, which are elastic collision, i.e. the sum of the kinetic energies of the colliding particles is the same before and after the collision. The volume and shape of the gases depends on the volume and shape of the container, where are located.

The change of the phase (solid, liquid, gaseous, plasma) of materials are called phase transitions. They are melting – change of solid to liquid, evaporating – liquid to gaseous and sublimation – solid to gaseous phase. These phase transitions are so called first order phase transitions, where the heat capacity of the material have a singularity, i.e. it is not defined. It is not defined, because despite the fact, that the material is heated ($\Delta Q \neq 0$) its temperature is not increasing. It means, that the received heat is not transformed into a temperature rise, but to the change of the state of the material. The relation between the absorbed (released) heat and the temperature is:

$$dQ = c_p dT \qquad dQ = mc_{mp} dT \qquad dQ = nc_{np} dT \qquad (1)$$

where c_p , c_{mp} , c_{np} is the heat capacity of the system, specific heat capacity and molar heat capacity, respectively, Q is the heat received (released) by the material, T is the thermodynamic temperature

1 Boiling of Liquids

Boiling point, temperature at which the pressure exerted by the surroundings upon a liquid is equalled by the pressure exerted by the vapour of the liquid; under this condition, addition of heat results in the transformation of the liquid into its vapour without raising the temperature.

The liquid is changing to a vapour (gas). From the definition it is clear, that the boiling point depends on the surrounding pressure, increases with increasing pressure and depends on the purity of the material, also.

Usually, boiling points are tabulated at normal pressure (**101 325 Pa**), and expressed in Celsius degrees or in kelvins. The boiling points (t_v) measured at other pressures (p_b) as normal is necessary to correct according to the equation:

$$t_b = t_v + k(101325 - p_b) \text{ (}^\circ\text{C)} \quad (2)$$

Where t_b is the corrected boiling point and k is the correction coefficient listed in Table 1.

Specific heat (enthalpy) of vaporization (ΔH_{vs}) is amount of heat received by 1 kg of liquid at given pressure, which is necessary to transform the liquid to its saturated vapour of the same temperature. Unit J kg^{-1} .

Molar heat (enthalpy) of vaporization (ΔH_{vm}) is amount of heat received by 1 mol of liquid at given pressure, which is necessary to transform the liquid to its saturated vapour of the same temperature. Unit J mol^{-1} .

$$\Delta H_{vm} = \frac{\Delta H_v}{n} \text{ (J mol}^{-1}\text{)} \quad (3)$$

where ΔH_v is the heat required to evaporate the liquid and n is the amount of the liquid.

The relationship of the temperature of the phase transition in equilibrium (in this case vaporization) is expressed with the Clausius-Clapeyron's equation:

$$\frac{dp}{dT} = \frac{\Delta H_{vm}}{T(V_m^g - V_m^l)} \quad (4)$$

where p is the pressure of surroundings (Pa), T is the boiling point (K), V_m^g and V_m^l are the molar volumes ($\text{m}^3\text{mol}^{-1}$) of gaseous and liquid phases, respectively. The molar volume of the liquid phase is negligible in comparison with the molar volume of the gaseous phase (at normal pressure) $V_m^l \ll V_m^g$, so the difference of the molar volumes can be replaced with the molar volume of the vapour (V_m^g) and substituting for the molar volume of the vapour from the ideal gas law $V_m^g = \frac{RT}{p}$ we obtain the Clausius-Clapeyron relation in differential form:

$$\frac{dp}{dT} = \frac{\Delta H_{vm} p}{RT^2} \quad (5)$$

After integration we obtain the relation of the boiling temperature on the pressure of a liquid:

$$\ln \frac{p_2}{p_1} = \frac{\Delta H_{vm}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

where T_1 and T_2 are the boiling points (in K) of a liquid at pressures p_1 and p_2 , respectively.

Aim of exercise

To determine the boiling points of unknown liquids and to calculate the corrected boiling points to normal pressure.

Equipment

Apparatus to determine the boiling point for liquids (Figure 1).

Chemicals

Liquids to determine the boiling point.

Experimental procedure

The apparatus to measure the boiling point of a liquid shown in Figure 1 consists of evaporating vessel **1**, electrical heating body connected to a control unit **2**, vapour guide pipe **3**, thermometer **4**, cooler **5**, collector of condensed phase **6**, discharge valve for condensed phase **7**, overflow pipe **8**, discharge valve for liquid phase **9**.

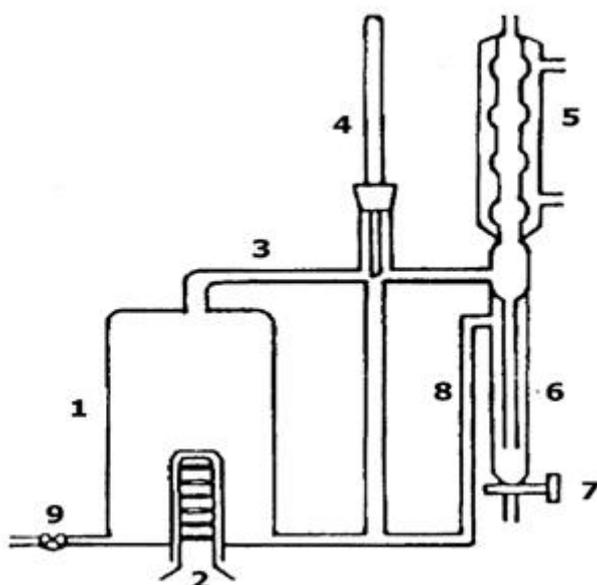


Figure 1 The apparatus to measure the boiling point

1. Fill the apparatus with the first liquid through the hole for the thermometer. The surface

level of the liquid in the evaporating vessel **1** should be 1 cm above the heating body. Place back the thermometer to the hole.

2. Connect the wires of the heating body to the control unit **2**. Put the output voltage on the control unit to 12-14 V (see arrows on the control unit).
3. Open the water valve for cooling water in the cooler **5**.
4. The heating body bring the liquid to a boil. The vapours pass through the guide pipe around the thermometer to the cooler **5**, where are cooled and condensed. The condensed vapours are collected in the collector **6**. When the amount of the condensed vapours reaches the open of the overflow pipe, they flow back to the evaporating vessel **1**. After certain time (10-15 minute), when the equilibrium is achieved, the temperature on the thermometer will display constant boiling point of the liquid. Write to the Table 1. the boiling point of the liquid (t_b).
5. Switch off the heating of the apparatus (set output voltage on the control unit to zero, unplug the wires of the control unit from electricity), pour back the liquid to the stock flask through the valves **7** and **9** (carefully lift and tilt the apparatus to remove the whole amount of the liquid through the valve **9**).
6. Do not rinse the apparatus with any liquid! Repeat the procedure and measure the boiling point of the remaining liquids!

Table 1 Determination of the boiling point of liquids

$p_b = \dots\dots\dots Pa$

Liquid	Measured t_v (°C)	$k \cdot 10^4$	Corrected boiling point t_b (°C)	Tabulated boiling point (°C)]

Data treatment

Fill in Table 1

- The atmospheric pressure (p_b) in Pa, which is available on the barometer in the laboratory.
- Correction coefficients (k) of liquids from Table 2 on the end of the manual.
- The corrected boiling points of liquids (t_b) according to equation 2.
- Tabulated boiling points from the handbook (ask your teacher for the handbook).

Table 2 Correction coefficients (k) of liquids

Liquid	$k \cdot 10^4$	Liquid	$k \cdot 10^4$
acetone	2.9	chlorophorm	2.9
amylalcolhol	2.3	cresol	3.2
benzene	3.2	acetic acid	3.3
ether	2.7	ethyl acetate	3.3
ethanol	2.5	methyl salicylate	4.3

Conclusion

In the conclusion compare the calculated (measured) and the tabulated (from the handbook) corrected boiling points.

2 Melting point of solids

Melting point (t_t) is defined as a temperature, where the liquid and solid phases of a material coexist in equilibrium at the given pressure.

Heating a solid, chemically pure substance, the temperature of the material is increasing (see Figure 2) up to certain temperature, when a melted portion (liquid phase) of the material occurs next to the solid portion. This temperature is called the melting point.

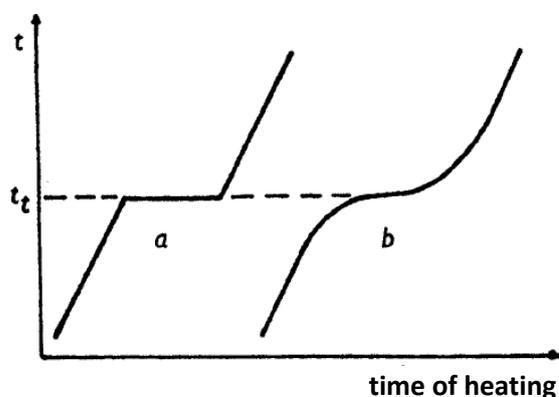


Figure 2 Change of melting temperature substance by heating
a – chemically pure substance
b – chemically impure substance

When the heating of the pure substance continues, the added heat is consumed to melt the solid part of the material until the whole amount is transformed to a liquid and up to this moment its temperature is stable. This appears as a horizontal part (plateau) on the heating curve (Figure 2a). As the whole amount of the material is melted, the heating results further increase of the temperature. (part *a* and *b* on the Figure 2).

In the case of melting of a chemically impure substance, the breaks on the curves are not so

sharp (part *b* on the Figure 2) as in the case of a pure substances. The melting of an impure material occurs within a temperature range (interval), where the width of this interval depends on the amount and quantity of the impurities.

Specific melting heat (enthalpy) (ΔH_t) is the amount of the heat necessary to melt 1 kg of a solid material at temperature of the melting point to liquid of the same temperature at the given pressure. The unit of the specific melting heat is $J\ kg^{-1}$.

Molar melting heat (enthalpy) (H_m) is - amount of the heat necessary to melt 1 mole of a solid material, at temperature of the melting point, to liquid of the same temperature at the given pressure. The unit of the specific melting heat is $J\ mol^{-1}$.

$$\Delta H_{tm} = \frac{\Delta H_t}{n} \quad (7)$$

n is number of moles.

During solidification of a liquid (reverse process of melting) the same amount of heat is released as during the melting, but the sign of ΔH is opposite. The melting point depends on the pressure in the environment and it was expressed by Clausius in differential form:

$$\frac{dT}{dp} = \frac{T(V_m^l - V_m^g)}{\Delta H_m} \quad (8)$$

where T is melting point of the material (K), p is pressure of the environment (Pa), V_m^l , V_m^g are molar volumes of the liquid and gaseous phases ($m^3\ mol^{-1}$), respectively.

The melting point is measured with a Kofler block (Figure 3). During the determination of the melting point with a Kofler block, the material is inspected continuously while its temperature is increasing. The beginning and the end of the melting of the crystallites is recorded, which corresponds to the interval of the melting of the solid materials. The width of this interval depends on the purity of the material.

Description of the Kofler block

The Kofler block consists of a heating part, where the sample is heated, a microscope to observe the changes and of a control part with a display to register the temperature and to control the apparatus.

Aim of exercise

To determine the melting points of solid materials

Equipment: Kofler block

Chemicals: Series of solid samples



Figure 3 Kofler block and capillaries for melting point measurements

Experimental procedure

Follow the manual placed next to the apparatus.

Conclusions

Compare the measured melting points with the tabulated values.

Reference

Oremusová J., Vojteková M., Sarka K.: Fyzika – laboratórne cvičenia pre farmaceutov UK Bratislava 2009 (in Slovak).

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