LIQUID-VAPOR EQUILIBRIUM CURVE AND VAPORIZATION ENTHALPY

1. PURPOSE OF THE WORK

Determination of the liquid-vapor equilibrium curve and the enthalpy of vaporization for water.

2. THEORETICAL NOTIONS

In the case of the vapor equilibrium (liquid-vapor) for a single-component system, knowledge of the pressure or temperature is sufficient for the system to be determined, in other words, a certain boiling point corresponds to a single value of the vapor pressure.

The variance of the system results from the law of phases:

$$v = c - f + 2 \tag{1}$$

where v - the number of degrees of freedom (variables), c - the number of components and f - the number of phases.

In the case of a pure substance (water), the number of variables that must be known to define the system is therefore: $v = 1 - 2 + 2 = 1$ *(univariant)*.

In the state diagram of the substance **the vaporization curve** starts at the triple point and ends at the critical point. The differential equation of this curve is expressed by the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta^{v} H}{T \Delta V} \tag{2}$$

in which $\Delta^{v}H$ is the enthalpy of vaporization at temperature T;

ΔV - the volume variation of the system in case of the considered transformation:

$\Delta V = V_g - V_l$

where: V_g - molar volume of the gas phase, V_l - molar volume of the liquid phase.

In a temperature range quite far from the critical temperature (for water this is Tc = 647 K), where $V_g >> V_l$ and the vapors have ideal behavior, we have:

$$\Delta V = V_g = \frac{RT}{P}$$

With this modification, for one mole of substance, equation (1) takes the form

$$\frac{d \ln P}{dT} = \frac{\Delta^{v} H}{RT^2} \tag{3}$$

known as **the Clausius-Clapeyron equation**.

For small temperature ranges, in which $\Delta^v H$ can be considered practically constant, by integrating equation (2) is obtained an expression of the type:

$$\ln P = \frac{A}{T} + B \tag{4}$$

where it was noted $A = -\frac{\Delta^v H}{R}$.

Hence for the vapor pressure an exponential temperature dependence, given by the equation below:

$$P = \exp\left(\frac{A}{T} + B\right) \tag{5}$$

Using the integrated form of the Clausius-Clapeyron equation it is possible to calculate the enthalpy of vaporization if the dependence of temperature vapor pressure is known.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- distillation flask, thermometer, condenser, buffer vessel, differential pressure gauge and a water aspirator.

3.2. PROCEDURE

The principle of the method

The principle of the Ramsay-Young method for determining the vapor pressure is as follows: a certain pressure is kept constant and the temperature at which the water boils is determined, under the set pressure.

The distillation flask heats up slowly. For the correct recording of temperatures, the thermometer tank must be continuously moistened by condensing vapors, so it is placed just below the neck of the condenser. The distillation flask is half filled with distilled water, to which a few pieces of porous porcelain are added to prevent overheating and ensure uniform boiling (usually this operation is no longer performed because the flask is already fixed in the installation).

Then the manometer is turned on.

Open the tap that connects to the water aspirator and as much air as possible is removed from the installation. When the desired pressure value is reached, close the valve, turn on the heating nest and read the temperature when the water boils, which is indicated by maintaining a constant temperature. (If it does not stabilize in about 5 minutes from the beginning of boiling, and the pressure value indicated by the manometer varies, it means that the installation is not sealed, in which case the heating is stopped, the sealings are checked again, the vacuum is restored in the installation, after which restarts heating).

Note the constant pressure corresponding to *P*. The value of this pressure is given by the relation

$$P = P_a - \Delta l \tag{6}$$

where P_a - atmospheric pressure and Δl - the value indicated by the differential manometer.

After performing the first determination, lightly open the valve that now connects to the air (as water is turned off) and introduce air into the installation, thus changing the pressure in the system by only 20-25 units. The new vaporization equilibrium is expected to be established, the temperature being monitored until it becomes constant again. Note the new constant temperature and pressure values.

For the following determinations, proceed similarly, always increasing the pressure in the system in small increments, by slightly opening the valve. The last measurement is made at a pressure equal to atmospheric pressure.

If the pressure gauge display closes, it must be restarted (it keeps all the initial settings without the closing/starting affecting the measurements) or if it displays strange values during the measurements the battery should be replaced.

4. EXPERIMENTAL DATA PROCESSING

4.1. Experimental pressure-temperature data are tabulated:

No.	***t*, °C**	***T*, *K***	***1/T*, K^{-1}**	**Δl, mbar**	**$P = P_a - \Delta l$ mbar**	**ln P**
1.						
2.						
3.						
…						

4.2. The vapor pressure *P* is calculated based on the relation (6), in which the value of the atmospheric pressure P_a is provided by the teacher or can be considered **1013.25 mbar** (the value of the atmospheric pressure under normal conditions);

4.3. Draw the experimental vapor pressure curve as a function of temperature *P* = f (*t*), whose dependence is given by equation (4);

4.4. The natural logarithm of the vapor pressure is plotted as a function of the inverse of the absolute temperature, $\ln P = f\left(\frac{1}{T}\right)$;

4.5. Calculate the enthalpy of water vaporization, $\Delta^v H$, from the slope of the line obtained in section 4.4, denoted by *m*, $\Delta^v H_T^o = -R \cdot m$;

4.6. Calculate $\Delta^v H$, by analytical method, based on the data in the table (taking data pairs as far apart as possible) and averaging 3 such values:

$$\Delta^v H_T^o = \frac{R \cdot \left(\ln P_2 - \ln P_1\right)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

4.7. Compare the values obtained in points 4.5 and 4.6 with the value in the literature, calculating the percentage errors.

Data from the literature

$$\Delta^v H_{H_2O} = 40680 \text{ J/mol} \qquad ; \qquad R = 8{,}314 \text{ J/(mol K)}$$

5. QUESTIONS

5.1. What is the influence of pressure on the boiling temperature of a liquid? Give examples.

5.2. How can the water vaporization curve be used to determine atmospheric humidity?