DETERMINATION OF THE MOLAR HEAT OF VAPORIZATION FOR WATER AT THE BOILING TEMPERATURE

Work objective: experimental determination of the molar heat of evaporation of water at atmospheric pressure and boiling point; calculation of van der Waals constant.

Equipment and accessories: instrument for determining the molar heat of vaporization, AC amvoltwattmeter, power supply, graduated cylinder or analytical balance, stopwatch, glass, glass of small capacity.

INTRODUCTION

Evaporation of a liquid requires heat. In order for the liquid to evaporate isothermally, to the unit of mass of the liquid must be supplied a certain amount of energy, which is called the specific heat of vaporization λ. To evaporate one mole of liquid the molar heat of vaporization λ_M is required. In accordance with the first law of thermodynamics, the heat input dQ is consumed to change the internal energy of the system dU and to perform the work of pdV to expand the volume of the liquid when it evaporates:

$$dQ = dU + pdV.\tag{1}$$

The internal energy of a real gas depends not only on temperature, but also on volume. According to the van der Waals model, the potential energy of a mole of gas or liquid is inversely proportional to the volume V:

$$E_n = -\frac{a}{V}.$$

with a − the van der Waals constant which depends on the matter itself and its temperature. So, vaporization of 1 mole of liquid requires energy:

$$\lambda_M = a\left(\frac{1}{V_{liq}} - \frac{1}{V_n}\right) + P\left(V_n - V_{liq}\right),\tag{2}$$

where V_{liq} is the molar volume of the liquid, V_n is the molar volume of the vapor.

Given that $V_{liq} = -\dfrac{M}{\rho_{liq}}$ (M – molar mass, ρ_{liq} – liquid density, and vapor can be considered an ideal gas) and that $V_{liq} << V_n$ (if far from the critical temperature), the molar heat of vaporization can be approximately calculated using the formula that follows from the formula (2):

$$\lambda_M \approx \frac{a\rho_{liq}}{M} + RT .\qquad(3)$$

In this practical, the λ_M value for water is measured at the boiling point and at the atmospheric pressure (information about the processes occurring in liquids at boiling is given in the appendix to this description).

Heat is transferred to water from an electric heater through which the alternating current flows. Passing through the heater during time τ, the electric current does a work $A_1 = P_1\tau$, where P_1 is the power of the heater.

In stationary mode, when the temperature of the liquid is equal to the boiling point, all the power is applied to turn the water into steam and to heat the environment (heat losses), that is,

$$P_1\tau = \lambda_M \nu_1 + q .\qquad(4)$$

Where ν_1 is the number of moles of water evaporated during time τ, q is the heat loss during this time. A similar equation can be written for another stationary mode characterized by a different power value P_2 of the heater. If the evaporation time is the same as in the first case, then the heat loss is the same, therefore

$$P_2\tau = \lambda_M \nu_2 + q .\qquad(5)$$

Comparing (5) and (4), we obtain the expression for calculating the molar heat of vaporization:

$$\lambda_M = \frac{\tau(P_1 - P_2)}{\nu_1 - \nu_2} .\qquad(6)$$

DESCRIPTION OF EXPERIMENTAL SETUP

A photograph of the device for determining the molar heat of vaporization of water is shown in Figure 1.

The vessel *1* with water is tightly closed with a lid *2*. Through the lid, one has placed leads of the heater *3*, as well as the tube *4* which removes steam to the condenser *5*. Cold water is supplied to the condenser walls via in and out nozzles. The steam generated during the boiling of water, passes through the condenser, turns into water, which is collected in a glass *6*. The power supplied to the heater is regulated by tuning the voltage regulator knob and measured with a wattmeter.

Measuring instruments (ampere-volt-wattmeter, stopwatch, analytical balance or graduated cylinder) allow you to find the values of all quantities which are necessary for the experimental determination of λ_M.
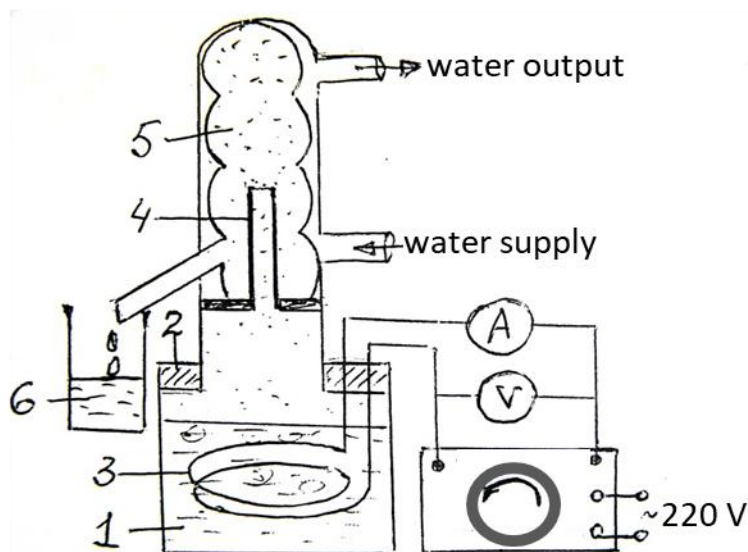

Figure 1. Experimental setup

MEASUREMENT AND DATA PROCESSING
Preparing the experimental setup

Check that the water in the vessel *1* is well above the heater *3*. Open the central red tap connecting the system to the water supply. Opening the blue valve slowly, let the cold water into the condenser.

Check readiness of the ampere-volt-wattmeter: for power measurement, the "Π_2" switch (see photo to the left) should be set to the "W" position. Voltage limit is set to "300 V". Switch "Π_1" must be set to "2.5 A". In this case, the maximum power measured by the device equals to 300V·2.5A = 750W. The power is read out using the upper scale "W" (photo below).

Connect the electrical circuit (with the permission of the teacher or laboratory technician) and set the power to 500 W in the heater circuit using the power supply. Start the measurement allowing 5-7 minutes for system to warm up and achieve a steady state boiling process.

Task 1. Measurements and calculation of the molar heat of vaporization for water

Collect condensed water in the glass *6* over a period of time $\tau = 80$ seconds. Measure the time τ of condensate collection with a stopwatch. **It must be the same for all the measurements (or renormalization should be applied)!**

When you are done with collecting of the condensate, set a different power value (400 W) so that the setup is ready for the next measurement. While a new stationary regime is being established (within 5-7 minutes), measure the mass of the water collected using a measuring glass or analytical balance scale (which provides you a more accurate result). Calculate the number of moles ν of the evaporated water. Make such measurements at four different values of power (500, 400, 300, 200 W), but for the same collecting time $\tau = 80$ s.

Fill in the table using results of the measurements.

№	*P*, W	*m*, mg	ν, mole	
1	500			
2	400			$\tau = 80$ s
3	300			
4	200			

Calculate λ_M using formula (6) and estimate the error of the result. Calculate the specific heat of vaporization of water $\lambda = \dfrac{\lambda_M}{M}$ and compare the obtained value with the table value which is $\lambda_{table} = 2.25 \cdot 10^6 \ J / kg$.

Task 2. Calculation of van der Waals constant *a*

Using formula (3), find the value of the van der Waals constant *a* for a mole of water and compare the value obtained with the table one ($a = 5.52$ atm·l²/mole). For comparison, translate this value into SI.

QUESTIONS AND EXERCISES

1. Why does the temperature of a liquid not change at boiling at constant pressure?

2. How to explain, from the molecular-kinetic theory point of view, the decrease in the molar heat of evaporation with increasing temperature? What is the heat of evaporation of water at a critical temperature?

3. Using formula (3), determine which part of the heat of evaporation at 100°C is used to increase the internal energy, and which to do an external work.

4. Write down the van der Waals equation and explain the meaning of the corrections contained in it. Draw in coordinates *(p, V)* the van der Waals isotherms and experimental isotherms of real gas.

5. What is the critical state of matter? How are critical parameters calculated in the van der Waals model?

6. Draw a diagram of the phase equilibrium H_2O in the coordinates *(p, T)*. Indicate on it the areas corresponding to the solid, liquid and gaseous states.

7. Obtain the theoretical *p(T)* relationship for the saturated vapor pressure, considering steam as an ideal gas.

8. Using the Clapeyron – Clausius equation, calculate at what external pressure the water boiling point will be 95°C? 105°C?

9. What is superheated fluid? Supersaturated steam? How can such states of matter be obtained?

APPENDIX
ABOUT BOILING OF A LIQUID

It is known that evaporation of a liquid can occur at any temperature. The presence of the atmosphere, however, significantly affects the picture of the process. Evaporation looks completely different, depending on whether the pressure of saturated vapor at p_V at a given temperature is less than or greater than the external atmospheric pressure p.

If $p_V < p$, relatively slow evaporation from the surface occurs. If p_V reaches (or slightly exceeds) the pressure of the surrounding atmosphere, **boiling** of the liquid occurs. In this case, vaporization occurs in the entire volume of the liquid. The centers of vapor formation are the smallest bubbles of extraneous gases, usually existing on the walls of the vessel (or on the dust particles suspended in the liquid). The liquid evaporates into the gas bubble, so the bubble is filled not only with gas, but also with saturated steam.

As the temperature rises to a certain value, the volume of the bubble becomes such that Archimedean force causes the bubble to afloat, leaving the embryo of the new bubble on the wall. The residual bubble is not in equilibrium, since the internal pressure in it exceeds the external one, therefore it quickly swells and re-emerges. The liquid boils. If a liquid boils at a constant external pressure, then its temperature remains unchanged during the entire boiling process.

The boiling of a liquid can be achieved either by heating the liquid at a constant pressure, or by changing the external pressure at a constant temperature (for example, when pumping air through the pump, water can boil at room temperature).

At each given pressure, water will boil at the temperature at which the pressure of its saturated steam is equal to the external pressure. It follows that the graph *P(T)*, representing the temperature dependence of the saturated vapor pressure, also determines the pressure dependence of the boiling point.