

3. Thermochemical measurements

3.a. Determination of temperature dependence of evaporation heat from the vapour pressure of the liquid



The temperature dependence of the saturated vapour pressure logarithm $\ln p$ of the pure liquid can be expressed by the Clausius-Clapeyron equation in differential form

$$\frac{d \ln p}{dT} = \frac{\Delta H_V}{RT^2} \quad (3.1.)$$

where the molar evaporation heat ΔH_V depends on temperature T . However, if the monitored temperature interval is small ($< 5^\circ\text{C}$), the dependence of ΔH_V on temperature can be neglected and the eqn (3.1.) can be easily integrated. Thus we obtain as follows:

$$\ln \frac{p_2}{p_1} = -\frac{\Delta H_V}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3.2.)$$

where T_1 (in kelvins) is boiling point of the liquid at pressure p_1 and T_2 is its boiling point at different pressure p_2 .

The relationship between values p and T of the liquid at boiling point are also often described by the empirical equation of the linear type:

$$\ln p = A/T + C \quad (3.3.)$$

If the substances A and B have a similar chemical structure, we often find that the ratio $\Delta H_V^A / \Delta H_V^B$ at their evaporation

temperature is constant over a relatively wide temperature range. Under this assumption and using the equation (3.1.), we get the relation:

$$\ln p_B = \frac{\Delta H_V^B}{\Delta H_V^A} \cdot \ln p_A + C' \quad (3.4.)$$

where C' is the constant. This equation is the basis of the Cox-Othmer diagram (i.e. dependence $\ln p_B$ on $\ln p_{H_2O}$, where p_B and p_{H_2O} are boiling pressures of alcohol and water at the same temperature).

? **TASK:** Determine the vapour pressure of alcohols at their boiling temperature, including changes in molar evaporation heats within the observed temperature range. For each alcohol, determine the constants A and C of the empirical equation (3.3.). Construct the Cox-Othmer diagram (use tabulated values for p_{H_2O}).



✂ **LABORATORY AIDS AND CHEMICALS:** Apparatus as given in **FIGURE 1**. Rotary oil pump, water thermostat with temperature accuracy $\pm 0.1^\circ\text{C}$. Methanol, ethanol, propanol.

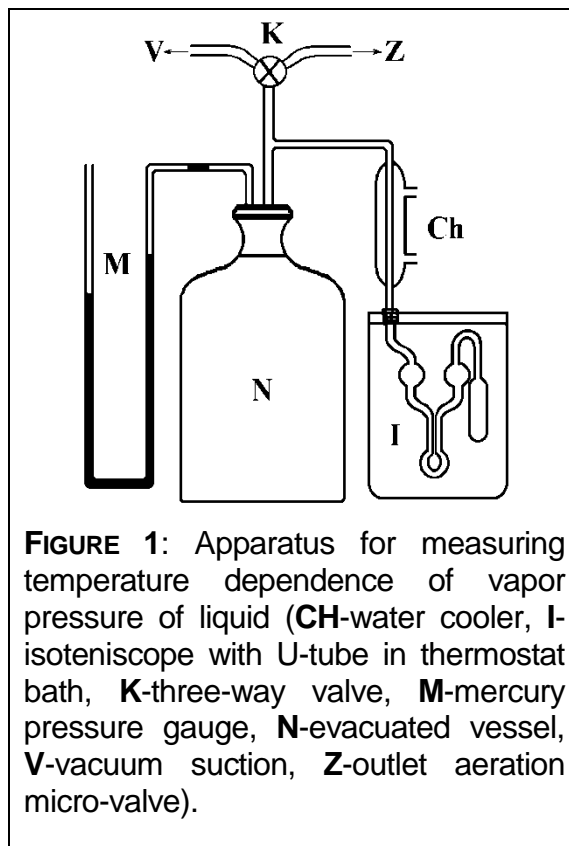


FIGURE 1: Apparatus for measuring temperature dependence of vapor pressure of liquid (**Ch**-water cooler, **I**-iseniscope with U-tube in thermostat bath, **K**-three-way valve, **M**-mercury pressure gauge, **N**-evacuated vessel, **V**-vacuum suction, **Z**-outlet aeration micro-valve).



INSTRUCTIONS: Check the apparatus as shown in **FIGURE 1**. When the isoteniscope is not filled, fill it carefully with pure methanol (ethanol or propanol) so that the cylindrical container is filled with two-thirds. Pour the alcohol into the U-tube with a pipette and then repeatedly tilt it to move the liquid into cylindrical section. We leave the last liquid portion in the U-tube. The liquid inside U-tube will serve as an overpressure indicator. According to **FIGURE 1**, connect the isoteniscope with the water cooler *CH*.

Let the water circulate inside the water cooler. Fill the thermostat bath with the water being cold as possible and set the thermostat control to the initial bath temperature (ie best below 15°C). Turn on the rotary oil pump, connect with vessel *N* by three-way valve *K*, and reduce the pressure inside the vessel until the alcohol starts to boil (ie a stream of bubbles passes through the U-tube).

As soon as alcohol is boiling (within approx. *2 min*) regularly, turn by three-way valve *K* so the vessel *N* is separated from the oil pump *V* and connected with an inlet aeration micro-valve *Z*.

Then start very slowly and carefully an opening the micro valve *Z* for an increase of the pressure inside apparatus. Your pressure sensor is given by the levels of the liquid inside isoteniscope U-tube. Fill up the vessel *N* with air using the micro valve *Z* until the levels inside U-tube of the isoteniscope be equalizing. At this moment, record exactly the difference in the mercury levels of the manometer *M* with a precision of 0.3 mm and note the temperature of the water inside bath with precision of 0.1°C

Make further measurements by increasing the bath temperature of the thermostat (step about 5°C for methanol, 4°C for ethanol, 3°C for propanol). The experimental procedure for measuring the equilibrium vapour pressure p of boiling alcohol at temperature T is the same as given before. Observe the boiling point of the methanol by this way up to a temperature that does not damage the used thermostat (for a poly acrylic bath it is about 60°C). Then fill the vessel with air using micro valve *Z*.

Replace the hot water in the cold in the thermostatic bath if you want to measure next alcohol. Then apply isoteniscope with a new alcohol liquid and repeat the measurement in accordance with the previous instructions.



IMPORTANT: It is not necessary for the vacuum pump to run at all times when the temperature in the bath is increased.

Do not forget to measure the laboratory pressure p_0 on the laboratory barometer. The difference between p_0 and the mercury level difference on manometer *M* is the vapour pressure p of the boiling alcohol at given temperature T . The dependence of the water vapour pressure on the temperature and the correct values of the evaporator heats of the alcohols are in the tables enclosed.



REPORT: laboratory pressure p_0 . **Table 1:** for each alcohol measured: equilibrium vapour pressure p (in both *torr* and *Pa* units), boiling temperature T (in $^{\circ}\text{C}$ and K), values $\ln p$, $1/T$ (K^{-1}), and ΔH_v ($J.mol^{-1}$) calculated using eqn (3.2.) valid between experimental temperature steps (5-3) $^{\circ}\text{C}$. **Common graph 1:** for all alcohols: dependence of $\ln p$ on $1/T$. **Table 2:** for each alcohol: the tabulated boiling point at standard pressure and evaporation heat ΔH_v , the confidence interval of the latent heat measured over whole experimental temperature interval, the parameters *A* and *C* of the experimental dependence (eqn (3.3.)), the boiling point at laboratory pressure p_0 calculated using eqn (3.3.). **Table 3:** for temperatures 0- 100°C (steps 5°C): value $\ln p_{H_2O}$, and $\ln p_B$ for all alcohols (here use the constant *A* a *C* for

calculations and apply eqn (3.3.)). **Common graph 2:** Cox-Othmer diagram for all alcohols including values $\Delta H_V^B / \Delta H_V^A$ and C' that were found as best linear fit.