

1.a. Construction of ethanol-water phase diagram



A pure liquid substance boils at a temperature at which its vapour pressure p_i^0 is equal to the pressure of the gas above it $p_i^0 = p_0$ (where p_0 is usually laboratory pressure). Experimental values of vapour pressures above pure liquid are usually given in tables (see **TABLE I**) or described by mathematical functions with experimental parameters. For ethanol it can be used:

$$\ln p_{et}^0 = 23,57999 - \frac{3674,37}{(t + 226,5)} \quad (4.1.)$$

where t is temperature in $^{\circ}C$.

A liquid mixture boils at pressure condition when its total vapour pressure p_c is equal to the pressure of the gas above it $p_c = p_0$. The total vapour pressure of the multicomponent liquid mixture is given by

$$p_c = \sum p_i^G \quad (4.2.)$$

where p_i^G are the equilibrium partial pressures of the constituents of the liquid mixture.

The equilibrium partial pressure p_i^G of the majority component i can be calculated using the **Raoult's law formula (RL)**:

$$p_i^G = x_i^L p_i^0 \quad (4.3.)$$

where molar fraction of majority component x_i^L is near 1.

On the contrary, if the component i in the liquid mixture is a minor component (ie $x_i^L \rightarrow 0$), its equilibrium partial pressure is governed by **Henry's law (HL)**:

$$p_i^G = x_i^L H_i^{px} \quad (4.4.)$$

where H_i^{px} is Henry's constant that is dependent on temperature, pressure, and composition of the liquid mixture.

Assuming the gaseous phase exhibits ideal behaviour (that is $p_i^G = x_i^G p_c$) and that the RZ is valid, the molar fraction of the component i in the gaseous phase x_i^G can be calculated using the known molar fraction of the component i in the liquid phase x_i^L as:

$$x_i^G = x_i^L \frac{p_i^0}{p_c} \quad (4.5.)$$

The calculated gaseous phase composition x_i^G deviates from the experiment for non-ideal mixture.

The Raoult's (Henry's) law cannot be generally used if the component is not a major (minor) component. We refer to the so-called positive deviation from the **RL** for component i if the calculated (use eqn. (4.3.)) partial pressure p_i^G is lower than the experimental partial pressure. Otherwise, the negative deviation from the **RL** is referred. We are talking about the predominance of the positive deviations from the **RL**, if the sum (see eqn (4.2.)) of the component partial pressures obtained using Raoult's law is less than the total experimental pressure (ie. if $p_c < p_0$ when liquid mixture boils in the distillation apparatus).

Liquid binary ethanol-water mixture can be distilled using a simple distillation apparatus in **FIGURE 1**. During the distillation of the liquid ethanol-water mixture, the liquid mixture boils at temperature T_B in the distillation flask and vapour rises to upper parts. The vapour is rich in more volatile component (here ethanol). The vapour liquefies at temperature T_A in the condenser and fall into reflux reservoir. The excess of the condensate (refluxing liquid) goes back to the distilling flask. After a certain reflux time, the temperatures T_B, T_A are nearly equal (if the insulation is good) and compositions in both distilling flask and reflux reservoir are different but stabilised (the chemical composition of steam and condensate in the reservoir is the same).

The composition of boiling mixture and condensed vapour can be determined from the phase diagram. The mixture of water and ethanol binary is an example of a non-ideal binary system (see phase diagram in **FIGURE 2**). If the mixture boils at temperature t_1 , the composition of the liquid mixture in the distillation flask (see point A in **FIGURE 2**) is x_{Et}^L . The composition of the vapour (see point B) is x_{Et}^G , and the overall composition of the system (see point O, ie. the composition of the mixture before heating) is x_{Et}^0 . Any change in the overall composition (for example condensate withdrawal) causes a boiling temperature change. The compositions of the liquid phase and the gas phase will change but always lie on phase boundary $L/(L+G)$ and $(L+G)/G$ respectively.

The mass of vapour relative to the mass of condensate is negligible thus the mass fractions of gaseous w^G and liquid w^L phases is governed by **the lever phase rule** that can be written in the form:

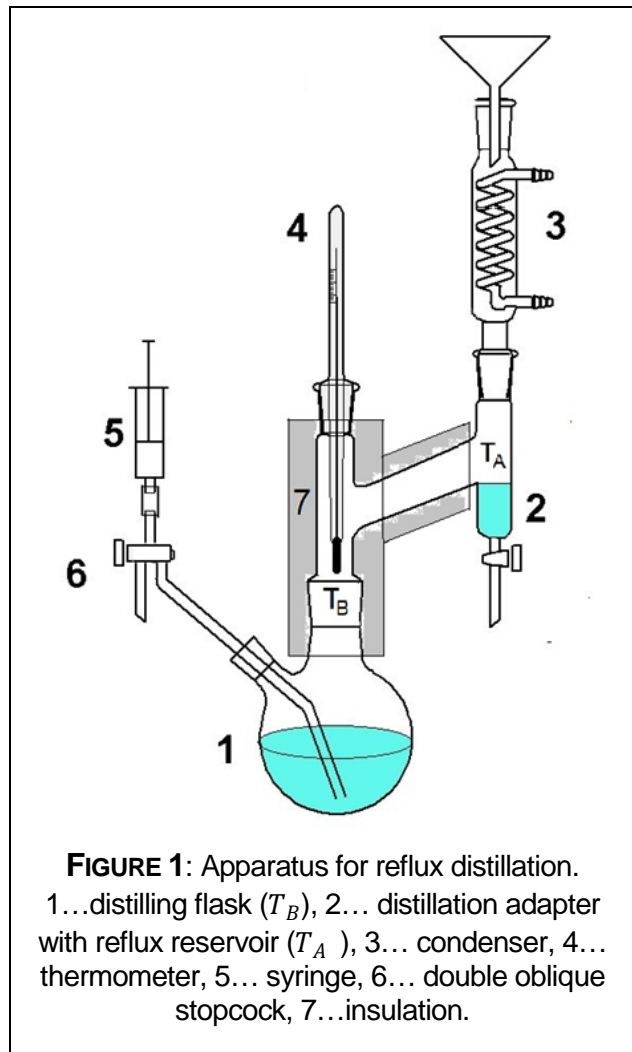


FIGURE 1: Apparatus for reflux distillation. 1...distilling flask (T_B), 2... distillation adapter with reflux reservoir (T_A), 3... condenser, 4... thermometer, 5... syringe, 6... double oblique stopcock, 7...insulation.

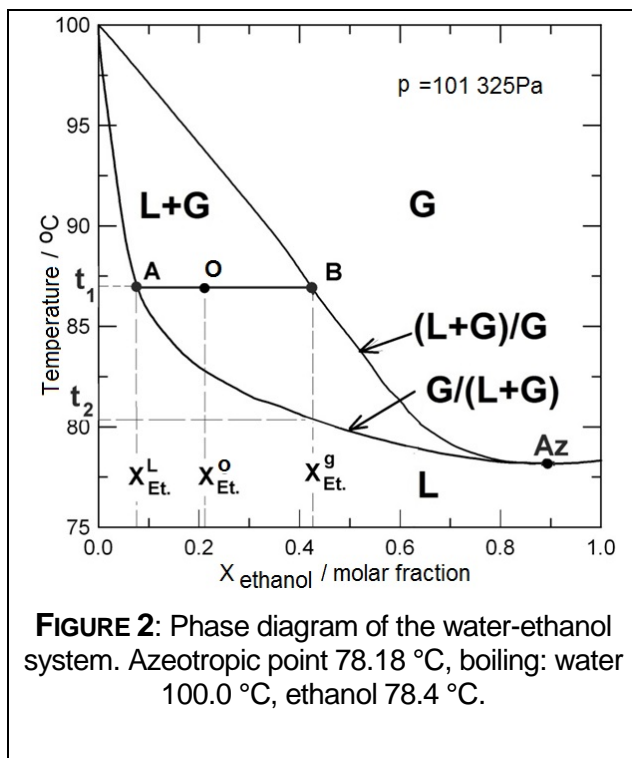


FIGURE 2: Phase diagram of the water-ethanol system. Azeotropic point 78.18 °C, boiling: water 100.0 °C, ethanol 78.4 °C.

$$w^G = \frac{m^G}{m^G + m^L} \quad \text{and} \quad w^L = \frac{m^L}{m^G + m^L} \quad (4.6.)$$

where m^G and m^L are the mass of the mixture in the reservoir and in the distillation flask respectively.



TASK: Determine the compositions of the co-existing gaseous and liquid phases during distillation of ethanol-water mixture at reflux conditions. Compare the experimental results with the phase diagram. Find out which deviation from the Raoult's law reveals the distilled mixture.



LABORATORY AIDS AND CHEMICALS: Apparatus for reflux distillation (see **FIGURE 2**, for main parts) including: thermometer (75-100 °C), spherical glass beads 3-5mm, laboratory heating mantle 1000ml, double oblique stopcock. 12 laboratory tubes, laboratory test tube rack, 2 syringes (20ml), 2 scale pipettes (5 and 10 ml). Distilled water, laboratory ethanol (95.6% by weight, preferably without denaturation). Oscillation densitometer. Ethanol-water standard mixtures with a molar ratio of ethanol: 0.05 (prepared by mixing 848 volumes of water + 152 volumes of laboratory ethanol); 0.10 (volume ratio: 723/276); 0.2 (534/466); 0.3 (396/605); 0.50 (207/793), and 0.70 (84/916).



INSTRUCTIONS: Assemble the distillation apparatus (see **FIGURE 1**). Insert several glass beads into the distillation flask and add ethanol-water mixture (250-300 ml). A suitable composition is about 50 vol% ethanol. You can also recycle the samples of the previous measurement.

1. Turn the inlet of cooling water to the condenser on. Switch on laboratory heating mantle. Bring the mixture to boil.
2. Let the mixture to reflux. Watch the temperature and wait for stabilization, then record the temperature T_B in the distillation flask and T_A in the distillation adapter (if is it at disposal).
3. Take the couple of the mixture samples. One from the distillation flask, the second from the reservoir to the separate test tubes.
4. Pour out so much distillate from the reservoir to let the mixture boil at temperature about 3 °C above the foregoing reflux temperature.
5. Continue according to point 2-4. Take out 6-7 couples of samples covering the 80-98°C temperature range.
6. Within free time during distillation, use the densitometer for measurements needed for a construction of calibration curve. You can also analyse the cold samples. Collect the samples and the calibration solutions for recycling. Measure density of both pure water and laboratory ethanol.
7. When the distillation has finished, switch off the heating mantle and turn the cooling water inlet off. Measure the air pressure in the laboratory.

Determination of calibration curve. Use pre prepared ethanol-water standards. Take a standard sample using syringe, rinse capillary of oscillation densimeter by first portion of the liquid standard, and leave the rest of the standard in oscillating capillary. Measure the density of all standard solutions, all samples, pure water and laboratory ethanol.



SAFETY: Do not leave the distillation apparatus without your supervising. Distillation is the most common cause of fires in laboratories.



REPORT: Calibration table 1: for each standard sample, water and laboratory ethanol: ethanol concentration in molar fraction x_{Et} , density ($g\ cm^3$).

Calibration graph 1: density vs. ethanol concentration x_{Et} . **Table 2:** for each sample taken from reservoir (G) and distillation flask (L): sample label (couple number completed with G or L symbol), sample density, ethanol concentration according to the calibration graph, temperature above distilling flask (T_A) or temperature near to condenser (T_B), the average of these temperatures for each couple. **Graph 2:** experimental phase diagram of binary system ethanol-water (like **FIGURE 2**, use average temperature for temperature on y-axis). **IN ADDITION:** laboratory pressure p_0 . **Table 3:** for pure ethanol, each sample and pure water: sample label, density, ethanol and water contents, boiling point (Find tabulated values for pure water and ethanol. Take average of T_B and T_A for refluxing samples.), ethanol p_{Et}^0 and water p_W^0 vapour pressures for samples in distilling flask at temperature equal to boiling point given in previous column (use **TABLE I** for pure ethanol and eqn (4.1.) for pure water), ideal partial pressures of constituents p_{Et}^G and p_W^G above liquid mixture calculated according Raoult's law (4.3.), sum $p_C = p_{Et}^G + p_W^G$, difference $p_C - p_0$, ideal ethanol content in gaseous phase $x_{Et}^G(ideal)$ (use eqn (4.5.)), difference $x_{Et}^G(ideal) - x_{Et}^G(exp.)$.

TABLE I: Saturated vapour pressures (in kPa) of water at different temperatures.

| T°C | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0 | 0.609 | 0.656 | 0.704 | 0.755 | 0.811 | 0.870 | 0.923 | 0.999 | 1.070 | 1.145 |
| 10 | 1.225 | 1.309 | 1.399 | 1.494 | 1.595 | 1.701 | 1.813 | 1.932 | 2.059 | 2.192 |
| 20 | 2.331 | 2.480 | 2.637 | 2.802 | 2.977 | 3.160 | 3.353 | 3.556 | 3.771 | 4.043 |
| 30 | 4.232 | 4.481 | 4.743 | 5.018 | 5.307 | 5.610 | 5.926 | 6.260 | 6.609 | 6.975 |
| 40 | 7.358 | 7.759 | 8.180 | 8.618 | 9.079 | 9.560 | 10.061 | 10.587 | 11.133 | 11.707 |
| 50 | 12.304 | 12.928 | 13.579 | 14.258 | 14.963 | 15.694 | 16.466 | 17.263 | 18.101 | 18.966 |
| 60 | 19.870 | 20.801 | 21.786 | 22.796 | 23.847 | 24.938 | 26.081 | 27.265 | 28.489 | 29.766 |
| 70 | 31.082 | 32.452 | 33.875 | 35.351 | 36.868 | 38.450 | 40.087 | 41.789 | 43.544 | 45.366 |
| 80 | 47.242 | 49.183 | 51.205 | 53.293 | 55.434 | 57.656 | 59.956 | 62.337 | 64.798 | 67.325 |
| 90 | 70.11 | 72.82 | 75.61 | 78.50 | 81.46 | 84.53 | 87.70 | 90.96 | 94.30 | 97.77 |
| 100 | 101.33 | 105.00 | 108.77 | 112.67 | 116.67 | 120.80 | 125.05 | 129.40 | 133.91 | 138.51 |