LABORATORY SESSION 6

Phase diagram: Boiling temperature - Composition of a binary liquid mixture

Material	**products**
2 vials	Methanol
2 spherical flasks two 50 mL mouths	Chloroform
3 rubber stoppers	Acetone for cleaning
2 cork bases	
4 dropper	
1 refractometer	
2 methanol and chloroform dispensers	
glass beads for boiling / 2 magnets	
1 distillation assembly / 1 heated magnetic stirrer / 1 NiCr-Ni thermocouple / 1 computer	

Objectives

1. Constructing the phase diagram, boiling temperature-composition of the methanol-chloroform mixture.
2. Determining the composition of the vapor phase (mole fraction) using the refractive index.
3. Determining the boiling temperature of binary mixtures.
4. Characterizing the azeotropic point (azeotropic composition) of the binary mixture.
5. Determining activity coefficients of the pure components and of the binary mixtures in liquid and vapor phases.

Theoretical background

a) Concepts:

Since we are going to build a phase diagram, we will start by defining the concept of **phase**: homogeneous part of a system. That is, part of the system whose macroscopic intensive thermodynamic variables (P, T, density, concentration, etc) have the same value in all that region, they are constant, they do not change. Thus, a heterogeneous system will be one formed by two or more phases, of the same component (pure substance) or of more than one component (mixture).

Therefore a **phase diagram** will be: a graphic representation that informs us in which phase or phases a component or several are in certain conditions (P, T, etc). The diagrams can represent pressure-temperature values (one component) or they can be pressure-composition at T = cte or Temperature-composition at P = cte in the case of mixtures of 2 or more components (binary, ternary, etc).

A particular type of mix is a **dissolution**: homogeneous mixture of two or more substances (components). The solutions can be classified in many ways, but from a thermodynamic point of view, and taking into account the interactions between their components, the solutions can be: ideal or real (not ideal).

In this practice, we are going to focus on liquid binary solutions (two components A and B); and in the study of the liquid-vapor balance (two phases).

b) **Ideal solutions:** laws, L – V equilibrium, diagrams.

A dissolution is ideal when the molecules of the different species are so similar to each other that the molecules of one of the components can replace those of the other without causing a variation in the spatial structure of the solution or in the energy of intermolecular interactions. In other words, A – A, B – B, or A – B interactions are of the same intensity.

Thermodynamically speaking, when the pure components go on to form an ideal solution, the mixing variables will be equal to the difference between the value of the magnitude in the solution and that of the pure components. So:

$\Delta V_M = 0$ there is no change in volume when the solution is formed, since the spatial structure does not change.

$\Delta U_M = 0$ the energy of the interactions does not change as the solution forms.

$\Delta H_M = 0$ no mixing heat at constant P: neither absorbs nor releases heat.

$\Delta S_M > 0$ disorder increases.

$\Delta G_M < 0$ dissolution formation is a spontaneous process.

An ideal solution is characterized in that it follows the **Raoult's law**:

$$P_i = P_i^0 x_i^L \qquad (1)$$

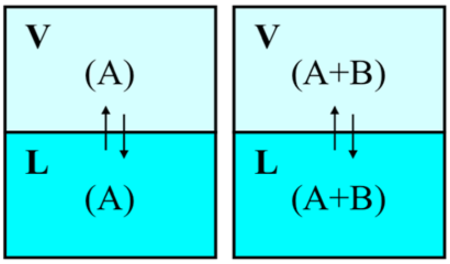
where i = A, B. Raoult's law gives us the vapor pressure of a component i (partial pressure, P_i) in the solution as a function of the vapor pressure of the pure component (P^o_i) and the mole fraction of the component in the solution (x_i^L) (at T_b = constant).

On the other hand the **Dalton's law** for ideal gas mixtures gives the partial pressure of each gas component (P_i) in the gas mixture as a function of the mole fraction of the component in the gas or vapor mixture (x_i^V) and the total gas pressure (P_T):

$$P_i = x_i^V P_T \qquad (2)$$

Combining ecs. (1) and (2) the composition of the vapor can be known through the composition of the liquid or vice versa, since the two do not have to be the same.

He **liquid-vapor equilibrium** (L – V) can be represented for a pure substance and for a binary liquid solution (in a closed system), as:



In this case, the **phase diagram** Boiling temperature - composition ($T_b - x$) of a binary liquid mixture (at P = constant) shows the compositions of the liquid and vapor phases of the mixture as a function of its boiling temperature. These diagrams are necessary when you want to separate both liquids by fractional distillation. Figure 1 shows the phase diagram of an ideal solution. In a constant pressure distillation experiment, the solution is heated, steam is extracted and condensed. The condensed liquid is richer in the more volatile component than the original liquid. Fractional distillation repeats the boiling and condensation cycle several times until the pure component is obtained.

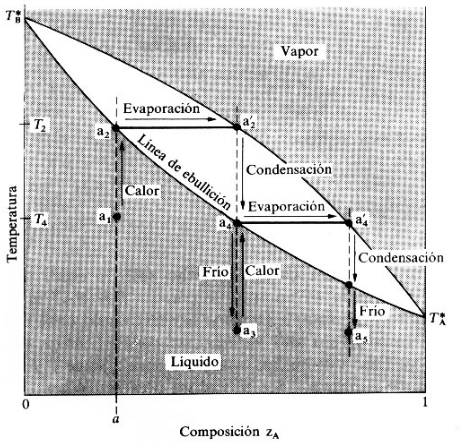


Figure 1. Phase diagram (liquid-vapor) temperature versus composition corresponding to an ideal mixture with A more volatile than B.

c) Real solutions: laws, L – V equilibrium, diagrams.

A real dissolution is one that does not obey an ideal behavior, that is, it does not comply with Raoult's Law and deviates from it positively or negatively because the interactions between its components are not of the same intensity, they are unfavorable or favorable.

In these cases, Raoult's Law must be modified with a **activity coefficient** (γ_i) that accounts for interactions:

$$P_i = P_i^o \, a_i = P_i^o \, x_i^L \, \gamma_i \qquad (3)$$

Combining equations (2) and (3), the expression of the activity coefficient is obtained:

$$\gamma_i = \frac{P_i}{P_i^o \, x_i^L} = \frac{P_T \, x_i^V}{P_i^o \, x_i^L} \qquad (4)$$

Actual solutions can show:

c.1) positive deviation from Raoult's law:

$\gamma_A > 1 \Rightarrow$ P_A (real) > P_A (ideal) $\Rightarrow \Delta G^{exc} > 0$ $\Rightarrow$ Unfavorable liquid A – B interactions.

In other words, the mixing process is not spontaneous (if $\Delta G^{real} > 0$). A-B interactions are less than A-A and B-B, therefore the molecules escape more easily from the solution to the vapor phase and their partial pressures will be higher than ideal (Raoult law). Furthermore, $\Delta H_M > 0$ and $\Delta V_M > 0$.

c.2) negative deviation from Raoult's law

$\gamma_A < 1 \Rightarrow$ P_A (real) $< P_A$ (ideal) $\Rightarrow \Delta G^{exc} < 0$ $\Rightarrow$ Favorable A – B interactions in the liquid.

In other words, the mixing process is spontaneous and therefore the liquid solution is stable. A-B interactions are greater than A-A and B-B. Furthermore, $\Delta H_M < 0$ and $\Delta V_M < 0$.

In this case, the dissolution is real and with a positive deviation, so the phase diagrams show a maximum on the curve P versus x on the pressure-composition phase diagram at constant temperature, fig. 2 (a) or a minimum on the T – x phase diagram, at constant pressure, fig. 2 (b). (Conversely, a negative deviation from Raoult's law produces a maximum on the T – x diagram.)

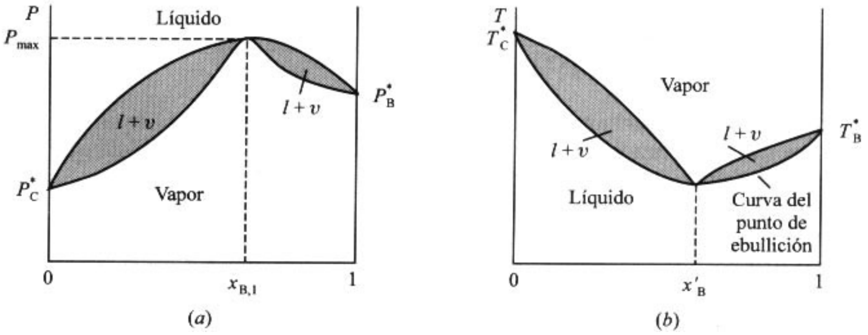


Figure 2. (a) Liquid-vapor phase diagram, pressure versus composition, with a maximum. (b) The corresponding diagram of temperature versus composition with its minimum.

The fractional distillation of these solutions gives a mixture whose composition corresponds to the maximum or minimum of the curve, where evaporation takes place without composition change. This mixture is called **azeotrope** (from the Greek "boiling without change"). Once the azeotropic composition is reached, the distillation cannot separate the two pure liquids. We will only get A pure and azeotropic or B pure and azeotropic. At the azeotropic point, the following is true: $x_i^L = x_i^V$. Example: ethanol-water (96% v / v ethanol).

d) Determination of the composition: from a physical property.

How are we going to determine the composition of our solutions to build the phase diagram? We will do this by measuring a physical magnitude of the solution: the refractive index, n. The **refractive index** (n = c / c ') is defined as the relationship between the speed of light in vacuum (c = constant) and the speed of light in the medium or solution (c'), which will depend on the composition of this medium.

Experimental procedure

Before starting the experience connect: the refractometer and the thermostatic bath at 20° C (if any), the water pump to cool the columns and the Cobra equipment (computer and potentiometer).

Do not use water throughout the experience.

PRECAUTIONS IN HANDLING THE REFRACTOMETER.

The surface of the refractometer must be cleaned and dried before each measurement.

Do not use aggressive substances or objects, they can scratch the surface of the refractometer.

There should be no bubbles inside the prism

1. Annotate atmospheric pressure (from the laboratory)
2. Measure the refractive index of a pure substance

   Put, with a dropper, a few drops of pure methanol on the surface of the prism of the refractometer and note its refractive index.

3. Determine the boiling temperature of a pure component and calibrate the temperature unit

   Introduce 20 mL of pure methanol into a 50 mL round flask with 6 or 7 boiling pearls and the magnet.

   Place the flask in the reflux assembly with the temperature probe. Start the hot plate and stirring **(moderate agitation and the magnet does not touch the thermocouple)**. Click on the "Measure" program icon and "start the measurement". When the temperature remains constant for at least one quadrant, calibrate.

   Remove the round-bottom flask from the distillation apparatus, remove the temperature probe and cool in the bath with the rubber stoppers on. When it is not hot, pour the contents into the waste container, collecting the pearls and the magnet.

4. Build the boiling temperature – composition diagram

   Methanol-chloroform solutions indicated in the Table are to be prepared successively in the two-neck flask (with boiling beads and magnet):

VMethanol (mL)	20	19	18	16	14	12	10	8	6	4	2	1	0.5	0
V Chloroform (mL)	0	1	2	4	6	8	10	12	14	16	18	19	19.5	20

With each solution, proceed as follows:

4.1. Measure the refractive index of the solution (n_L).

4.2. Place the flask in the reflux assembly with the temperature probe. Start the hot plate and stirring and start the measurement on the Measure program.

4.3. When the temperature remains constant for at least one quadrant (<u>note</u>), close the Teflon tap and extract a few drops of the condensate with the syringe without removing the needle, collect it in a vial and cool it in the bath. Reopen the Teflon tap.

4.4. Finish the measurement, determine the average temperature and <u>record</u> this temperature.

4.5. Remove the round bottom flask from the assembly, remove the stopper with the temperature probe, fit another stopper and refrigerate in the bath. When it is not hot, pour into the waste container

4.6. <u>Measure</u> the refractive index of the condensate (n_V).

5. <u>Measure the refractive index</u> of pure chloroform and its boiling temperature.

Treatment and Discussion of Results

1. <u>Calculate</u> the mole fractions of each component in the liquid mixtures.

<u>Data:</u>

	Methanol	Chloroform
d^{20} (g.cm^{-3})	0.7914	1.4832
n^{20}	1.3288	1.4459
M_r (g.mol^{-1})	32.04	119.32
T_b (ºC)	64.6	61.2

2. <u>Build</u> the composition calibration curve as a function of the refractive index, $x^L_{Metanol} = f(n^L)$of the methanol-chloroform solutions. Include the points corresponding to the pure components.

3. <u>Determine</u> the mole fractions of the components in the gas phase from the previous calibration curve. Include these results in the Table.

4. <u>Draw</u> the boiling temperature-composition diagram.

5. <u>Characterize</u> the azeotropic point. At that point, the two phases have the same composition, $\boxed{x_i^L = x_i^V}$.

   Therefore, if we represent the mole fraction of one of the phases against the mole fraction of the other, the azeotropic point must be located on the line that joins the points of equal composition in both phases. This graph is made for one of the components, for example methanol. The azeotrope point will be the one in which the obtained curve intersects the line that joins the points of equal composition in both phases.

   <u>Search for</u> in the bibliography (www.chemnetbase.com) the T and x (methanol) of the azeotrope and compare with the experimental result.

6. <u>Determine</u> the activity coefficients of methanol, chloroform and their mixtures from equation (4).

   Take the <u>atmospheric pressure</u> of the laboratory as value of total pressure. We also need to know the vapor pressure of a pure component as a function of temperature, which is given by Antoine's equation:

$$\log P_i^o = A - \frac{B}{C+T} \qquad (5)$$

where P_i^o it is expressed in hPa units, T is the temperature expressed in Celsius degrees and A, B and C are constants characteristic of each component:

	A	B	C
Chloroform	7.07959	1170,966	226,232
Methanol	8.20591	1582,271	239,726